MATERIALS SCIENCE APPROACH TO CHARACTERIZATION AND PREDICTION OF SENSORY TEXTURE IN CONFECTIONARY SYSTEMS

BY

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DISSERTATION

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Abstract

The food industry faces many challenges when attempting to formulate new or reformulate existing products to reduce sugar content. This problem is particularly pronounced in confectionary systems, such as caramels, in which sugar contributes the majority of sensory (i.e., sweetness, flavor, browning, texture) and physical (i.e., adhesiveness, structure) properties of the system. Sugar replacers can mimic some functional properties of sugar, but costly trial and error in reformulation is often required to achieve desired sensory and physical end-product properties. Matching product texture may pose a particularly steep challenge when replacing sugar in confectionary systems. Reliable instrumental prediction of sensory texture can supplement insight from sensory testing and streamline the reformulation process. Based on literature findings, accurate instrumental prediction of sensory texture has proven to be challenging. In order to meet this challenge, the goal of this research was to provide simple, reliable tools for the control of product texture through strategic formulation.

Caramel coating was identified as a promising model system for the development of instrumental predictors of sensory changes due to sugar replacement. In order to characterize the key categories of commercially available caramel coatings, a Napping-Ultra Flash Profile (Napping-UFP) study was performed with 12 commercial caramel popcorn samples. Hierarchical clustering analysis of the Napping-UFP data set for global, aroma-by-mouth, texture, and taste attributes resulted in the identification of 3 categories of caramel coatings: Small-scale Dark (SD), Large-scale Dark (LD), and Large-scale Light (LL). Compositional information from representative samples in each category was used to develop 3 model systems that matched the sensory properties of each category. The caramel coating model

systems were then manipulated by varying sugar replacer (isomalt, maltitol, mannitol, or sorbitol) and replacement level to achieve a wide range of textures.

Next, a descriptive analysis panel was utilized to generate a complete sensory profile of full- and reduced-sugar caramel coating samples. Principal components analysis (PCA) showed that aroma and aroma-by-mouth attributes of the samples were most strongly influenced by the model system (SD, LD, or LL), while texture attributes were most strongly influenced by the sugar replacer and replacement level used. Texture attributes of the caramel coating samples were then compared against a range of common instrumental metrics to test the usefulness of these metrics in predicting sensory effects of sugar reduction. Modest correlations were found between moisture content, water activity (a_w), and texture profile analysis (TPA) parameters and select texture attributes; however, glass transition temperature (T_g) showed the strongest correlations to sensory evaluations of texture attributes.

Evolution of full- and reduced-sugar caramel coating texture throughout mastication was then studied using the Temporal Dominance of Sensations (TDS) method and compared to both trained and consumer evaluations of stickiness in order to deepen understanding of stickiness perception and the effects of sugar replacement on texture. By correlating TDS dominance parameters and check-all-that-apply (CATA) selection rates with sample stickiness ratings, two tiers of stickiness-contributing attributes were identified. The texture attributes stringy, tacky, and enveloping comprised the first tier, showing significant positive correlations to stickiness by CATA and TDS, while attributes toothpacking, cohesive, and deformable comprised the second tier, showing significant positive correlations to stickiness only when multiple attribute

selections were allowed (CATA). Consumer and trained panelist evaluations of tactile and oral stickiness were congruent and highly, inversely correlated to T_g. Further, T_g proved to be a good predictor of textural trajectory, with samples for which T_g < room temperature (RT) following a trajectory from deformable to enveloping, and samples for which T_g > RT following a trajectory from brittle to toothpacking.

Given the power of T_g as an instrumental predictor of sensory texture attributes, the final phase of this research aimed to explore how thermal processing and T_g of ingredients relate to the T_g of a sample. The original and modified Couchman-Karasz equations were used to calculate an expected T_g (T_{CK}) for a range carbohydrate blends cooked to 120, 130, 140, and 150°C, and T_{CK} was compared to measured T_g. The T_{CK} calculated using the original and modified Couchman-Karasz equations deviated from measured T_g by an average of 20.1°C and 11.3°C, respectively. To improve the predictive power of the Couchman-Karasz equation, empirical corrections based on sample moisture content or final cook temperature were developed. Application of these corrections reduced the averaged difference between predicted and measured T_g to <5.6°C. Integration of the empirically modified Couchman-Karasz model with previously developed models for sample texture by T_g should enable prediction and strategic design of product texture. Further, this model should assist in the efficient formulation and process design of reduced sugar confectionary products through the use of T_g as a control parameter to minimize negative changes to product texture.

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Chapter 1: Introduction

1.1 Rationale and significance

Food material texture, and stickiness in particular, has proven to be difficult to predict instrumentally (Kilcast and Roberts 1998; Adhikari and others 2001). The most common instrumental predictor of sensory stickiness, physical adhesiveness, does not account for the complexity and dynamic nature of stickiness perception (Lenfant and others 2009). Traditional adhesiveness measurements made with texture analyzers fail to account for changes in temperature and moisture that occur during mastication. Texture analysis methods and probes also inadequately model mastication parameters and oral/dental surface properties (Dunnewind and others 2004). Finally, development of a method of stickiness prediction is challenged by the food context-dependence of stickiness perception, i.e., the variability in the understanding of stickiness between different food systems. A more reliable tool for instrumental prediction of sensory stickiness is needed. In order to develop a tool with relevance to the complete sensory perception of stickiness, the component texture attributes that contribute to stickiness perception in a given food system must be identified and measured.

A critical property in many food systems, stickiness is especially important in sugar-based coating systems where it plays both key functional and sensory roles (Kilcast and Roberts 1998). The intensity level and profile of stickiness must be optimized to ensure adequate adhesion to the food material it is coating, while limiting adhesion to packaging material or excessive adhesion to hand and oral surfaces. Achieving this fine balance is further complicated by the pressing issue of sugar reduction. Replacing sugar with reduced-calorie alternatives provides

additional challenges as sugar contributes to most functional and sensory properties of sugar-based coating systems (Alonso and Setser 1994). Short of performing comprehensive sensory testing on a range of reduced-sugar formulations, the product developer is unable to simply and accurately predict the sensory changes due to sugar replacement.

Glass transition parameters have previously been compared to sensory attributes of food products, including crispness and adhesiveness, as well as used as a guide to avoid the onset of stickiness in processing of spray-dried powders (Roos and Karel 1991; Huang and Hsieh 2005; Payne and Labuza 2005). However, glass transition parameters have yet to be used to directly predict sensory stickiness or temporal textural profile. The overall goal of this study was to bridge the gap between sensory and physical understanding of textural properties and stickiness in full- and reduced-sugar coating systems through correlation of sample texture with sample glass transition parameters. By creating a model for stickiness perception and textural profile of caramel coatings based on the thermal profile of sugars and sugar replacers used, this project will enable prediction and design of final product texture through control of the system glass transition temperature.

1.2 Objectives

It was hypothesized that stickiness intensity and dominance of contributing textural attributes in caramel model systems will systematically increase with decreasing glass transition temperature (T_g) of the caramel model systems. To test this hypothesis, the following four specific aims were examined:

Objective 1: Define key categories of commercially available caramel corn products through the use of the Napping-UFP flash descriptive profiling method to develop model caramel systems (Chapter 3).

Objective 2: Correlate sensory and analytical texture measures of model caramel systems to identify physical predictors of sensory properties (Chapter 4).

Objective 3: Identify textural attributes that contribute to stickiness perception and relate temporal profile of caramel texture to consumer perception of overall stickiness (Chapter 5 and 6).

Objective 4: Relate T_g and thermal profile to caramel sample texture profile by hand and by mouth and create a model of sample texture based on thermal properties and processing of ingredients (Chapter 6 and 7).

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Chapter 2: Literature review

2.1 Sugar replacement in foods

Motivation

Added sugars are gaining attention as a nutritional criterion, as evidenced by the addition of the key recommendation "to consume less than 10 percent of calories per day from added sugars" to the 2015-2020 Dietary Guidelines for Americans (U.S. Department of Health and Human Services and U.S. Department of Agriculture 2015). Predating this focus on added sugars, reducing total sugar consumption has long been a pervasive message in conversations around healthy diet and weight management (Gibson and Neate 2007). The relationship between sugar intake and weight gain or loss is not proven, as most recent reviews on the subject have concluded that calories from sucrose do not contribute to weight differently than calories from other macronutrients in healthy populations (Gibson 1996; Gibson and Neate 2007; Williams and others 2007; Clemens and others 2016). Similarly, sucrose has not been shown to be addictive as previously hypothesized (Benton 2010).

While recent publications show that the adverse health effects of sugar consumption are not as extensive as commonly believed, there are numerous health reasons to limit sugar intake. Positive correlations have been found between sugar intake and dental cavities (Heller and others 2001), as well as with the risk of development of type II diabetes (Koning and others 2011). Replacing sucrose in foods with high intensity sweeteners or sugar alcohols can reduce calorie consumption, the risk of dental cavities, and the glycemic index of foods, which has metabolic impacts for diabetic and pre-diabetic populations (Heller and others 2001; Koning and others 2011; Clemens and others 2016). Health reasons aside, sugar replacement in foods

is a compelling challenge due to strong consumer demand for lower-sugar products and support for labelling of added sugars on packaged foods (Kyle and Thomas 2014; Kim and others 2015).

Challenges

No single sugar replacer currently available can match the complex functionality provided by sucrose in foods and beverages (Alonso and Setser 1994). Consequently, a host of technical challenges accompany any effort to replace sucrose in products. Key sensory factors to consider when replacing sugar include matching the sweetness intensity and sensory profile of sucrose (Chattopadhyay and others 2014; Clemens and others 2016) and accounting for the color and flavor development contributed by sucrose through participation in caramelization and, following hydrolysis, Maillard browning reactions (Clemens and others 2016). Sucrose also provides critical structural and textural properties in foods and beverages. Products in which sucrose has been replaced by an alternative sweetener must also replace the mouthfeel or viscosity of sucrose-sweetened beverages (Kappes and others 2007; Clemens and others 2016) and the bulking and structure sucrose provides in solid and semi-solid foods (Alonso and Setser 1994; Chattopadhyay and others 2014; Clemens and others 2016). Texture is a particularly complex property to replicate in sugar-free or reduced sugar foods, as sucrose is capable of providing a wide array of texture attributes across diverse food systems depending on the state of sucrose in the system: crystalline, amorphous glass, amorphous rubber, or a combination thereof (Clemens and others 2016).

The impact of interactions of sucrose with water may be an overlooked functionality that sucrose provides. The colligative properties of sucrose, which cause both an increase in boiling

point and depression in freezing point, merit consideration in designing the processing parameters and storage conditions of products with reduced sugar content (Alonso and Setser 1994; Baek and others 2004; Clemens and others 2016). Sucrose also binds water effectively, adding humectancy to many products, most notably baked goods (Alonso and Setser 1994). Finally, sucrose lowers the water activity in foods, which may be a critical factor in ensuring the microbiological safety of a food product (Sleator and Hill 2007).

2.2 Sensory and functional properties of sweeteners

Mono- and disaccharides

Simple sugars comprise a vital category of ingredients to the food industry. They fulfill a number of significant functional roles, contributing sweetness, viscosity, bulking, and texture to food products (Monte and Maga 1982; Godshall 1995; Pihlsgard 1997; Godshall 1998; Colonna and others 2000). In addition to their innate properties, sugars provide development of flavors and colors through participation in chemical processes like the Maillard reaction and caramelization (Monte and Maga 1982; Pihlsgard 1997; Godshall 1998).

All sugars convey some sweet sensation, but the intensity, quality, and temporal profile of the sweetness varies by sugar (Portmann and Birch 1995; Clarke 1996; Godshall 1998; Godshall 2007). Relative sweetness values are compiled in Table 2.1, and sweetness intensity and persistence of sweet sensation versus concentration are presented graphically in Figures 2.1 and 2.2, respectively. The sweetness of sugars is not absolute, but rather depends on concentration, pH, temperature, matrix effects, stereochemical configuration, and the presence

of synergistic sweeteners (Godshall 1995; Portmann and Birch 1995; Pihlsgard 1997; Godshall 1998; Colonna and others 2000).

Sugars that show an increase in relative sweetness with increasing concentration are said to exhibit an expansion of sweetness with increasing concentration, while sugars that show the opposite trend are said to exhibit compression of sweetness (Portmann and Birch 1995). Figure 2.1 highlights the nature of fructose and sucrose to display compression of sweetness and of glucose, lactose, maltose, and trehalose to display expansion of sweetness with increasing concentration. While sweetness is often the key criterion in sugar selection, it is important to consider the complete sensory profile of each sweetener as well as its functionality within the specific food system when formulating a product (Chinachoti 1995; Colonna and others 2000; Godshall 2007). For example, the duration or persistence, of sweet taste sensation has been found to differ between sweeteners and concentrations, as shown in Figure 2.2 (Portmann and Birch 1995).

Sweet taste transduction

Simple sugars, such as monosaccharides and disaccharides, make up one class of a wide array of compounds that elicit a sweet taste (Brand and Feigin 1996). Sweet tastes are uniquely attractive to humans, stimulating pleasure centers in the brain and cueing the taster to consume the sweet food (Brand and Feigin 1996; Sugita 2006).

The transduction of sweet taste is a complex, multistep process, but decades of animal studies have illuminated a general schema. The process begins when a chemical stimulus, or sweet-tasting molecule, comes in contact with a sweet taste receptor protein on the surface of

taste buds located on the fungiform, foliate, or circumvallate papillae on the tongue and in the mouth (Norgren 1995; Brand and Feigin 1996; Lindemann 2001). G-protein-coupled receptors T1R2 and T1R3 have been linked to sweet taste recognition (Sugita 2006; Ohkuri and others 2009). Contact between the stimulus and the receptor protein initiates a cascade of biochemical events involving the stimulation of protein kinase A by the secondary messenger cyclic-AMP and the subsequent transmission of a neurological signal conveying the intensity and quality of the sweet sensation from the taste buds through the facial or glossopharyngeal nerves and to the gustatory cortex of the brain (Norgren 1995; Brand and Feigin 1996). This model is well-accepted as a mode of sweet taste perception, although knock out studies have proven that there are multiple parallel pathways of sweet taste transduction (Ohkuri and others 2009).

Sucrose

Sucrose is widely regarded as the gold standard for sweet taste and functionality and the sugar to which all other sweeteners are compared (Godshall 2007). A disaccharide composed of one glucose and one fructose unit, sucrose is a prevalent natural sweetener typically harvested from either sugarcane or sugarbeet and refined to a white, crystalline end product (Pihlsgard 1997; Colonna and others 2000; Godshall 2007). Cane sugar is the standard for the measurement of sweetness, with a relative sweetness score of 100 (Clarke 1996; Colonna and others 2000; Godshall 2007). Sucrose is perceived to be the sweetest at human physiological temperatures, 32 to 38°C, and exhibits a compression of sweetness as concentration increases (Figure 2.1) (Godshall 1995; Portmann and Birch 1995). The sweetness of sucrose can be enhanced by pairing it with one or more sweeteners with which it expresses

synergistic sweetness: fructose, glucose, xylitol, and other high intensity sweeteners as shown in Table 2.2 (Frank and others 1989; Godshall 1995).

Though off-odors are largely removed through the conditioning process, and the flavor of sucrose is generally described as purely sweet, some distinctive flavor volatiles often persist in beet and cane sugars (Monte and Maga 1982; Pihlsgard 1997; Godshall 1998; Grimm and others 2002). Sensory differences between sugars from beet and cane sources have been found and described (Monte and Maga 1982; Urbanus and others 2014). Urbanus and others (2014) demonstrated that panelists are able to differentiate between beet and cane sugars when evaluating the samples by aroma only and by aroma and taste together ($p < 0.05$), but not when evaluating by taste alone ($p = 0.19$). In a subsequent study, the sensory differences between beet and cane sugars from multiple sources were defined through a descriptive analysis panel (Urbanus and others 2014). Cane sugars were cleaner in flavor and characterized by a sweet aftertaste and fruity aroma-by-mouth, while beet sugars were found to carry more off-flavors and were characterized by earthy, barnyard, off-dairy, and oxidized aromas and by the aroma-by-mouth and aftertaste of burnt sugar (Urbanus and others 2014). This sensory study agrees with previous flavor chemistry research identifying flavor-volatiles present in beet and cane sugars (Godshall and others 1995; Pihlsgard 1997; Godshall 1998; Grimm and others 2002; Urbanus and others 2014). Cane sugars may carry a light caramel or sweet aroma, while beet sugars have been found to contain a much larger and more diverse group of aroma compounds contributing to cheesy, earthy, nutty, and caramel-like aromas, among others (Godshall and others 1995; Pihlsgard 1997; Godshall 1998).

In addition to carrying flavors from the raw source or refining process, sucrose has the ability to develop and deliver a wide array of flavor volatiles (Godshall 1995; Clarke 1996; Pihlsgard 1997; Godshall 1998). Exposure to heat at a range of time and temperature combinations can result in the caramelization of sucrose and generation of flavors and colors ranging from caramel-like, vanilla, and light-brown, to bitter, burnt, and dark brown to black (Monte and Maga 1982; Godshall 1998; Jiang and others 2008). Caramelization is generally desirable and produces pleasant aromas, but can result in undesirable sensory attributes as the degree of caramelization increases (Monte and Maga 1982; Godshall 1998). Sucrose may also be broken down, through heating, exposure to acidic conditions, or enzymatic hydrolysis, to fructose and glucose which serve as substrates in the Maillard reaction, a complex system of chemical reactions in which proteins react with reducing sugars to produce a vast array of flavor volatiles, including the caramel-like furans, Strecker aldehydes, licorice-like cyclopentenes, and nutty pyrazines, among others (Monte and Maga 1982; Pihlsgard 1997; Colonna and others 2000). Colors are generated in addition to flavors, as the Maillard reaction is also responsible for non-enzymatic browning. One of the by-products associated with the Maillard reaction is 4-methylimidizole, or 4-MEI, a carcinogenic compound that has garnered much press due to its presence in caramel coloring (Moon and Takayuki 2011). 4-methylimidizole has no documented sensory properties and is present in most Maillard browned products at only parts per million levels (Moon and Takayuki 2011). The Maillard reaction results in development of characteristic flavors and dark pigments that are essential to some food products and undesirable in others (Pihlsgard 1997).

Fructose

A prevalent and highly sweet monosaccharide, fructose occurs naturally in fruits and honey and as one half of the disaccharide sucrose (Colonna and others 2000). Fructose presents a clean, pure sweet taste with a reported mild fruity flavor (Clarke 1996). In its pure form, fructose is a white crystalline material, although it is more frequently incorporated into processed foods as a component of high fructose corn syrup (Colonna and others 2000). Fructose is an attractive ingredient because of its potency as a sweetener (Colonna and others 2000). The relative sweetness of fructose is highly dependent on concentration, temperature, and pH, with published relative sweetness scores ranging from 115 to 180 (Portmann and Birch 1995; Clarke 1996; Godshall 1998; Colonna and others 2000; Godshall 2007). Relative to sucrose, fructose is sweeter at lower temperatures and mildly acidic pH (Colonna and others 2000). The temperature effect was initially attributed to a dominance of the sweeter α-D-fructose over its anomer, β-D-fructose, in colder solutions (Pangborn and Gee 1961; Colonna and others 2000). However, subsequent studies suggest that the absolute sweetness of fructose is fairly constant as a function of temperature, and the increase in relative sweetness observed is due instead to a decrease in the sweetness of sucrose at low temperatures (Colonna and others 2000).

Like sucrose, fructose exhibits a compression of sweetness with an increase in concentration (Portmann and Birch 1995). The temporal sweetness profile of fructose differs from that of sucrose; fructose produces a much earlier peaking and faster fading sweet sensation (Portmann and Birch 1995; Colonna and others 2000). A rapid onset and fast fade make fructose an ideal sugar for accentuating other flavors in foods and a poor choice for

masking off-flavors or aftertastes (Colonna and others 2000). The sweetness of fructose can be maximized by combining the monosaccharide with one or more other sweeteners; fructose expresses a synergistic sweetness when mixed with sucrose or the high-intensity sweeteners sucralose, aspartame, saccharin, cyclamate, xylitol, and acesulfame K (Table 2.2) (Frank and others 1989; Colonna and others 2000).

Fructose also plays a role in the flavor development and texture of food systems. As a reducing sugar, fructose can participate in the Maillard reaction and contribute to flavor and color development in foods (Colonna and others 2000). Spies and Hosney (1982) demonstrated that the use of fructose affects the texture of baked goods, as fructose increases the starch gelatinization temperature in food systems to a lesser extent than sucrose (Colonna and others 2000). Depending on the food system in which it is incorporated, the greater relative sweetness of fructose can be lost, particularly when used at higher concentrations and in highly acidic solutions or baked/cooked systems (Cardello and others 1979; Godshall 1995).

Glucose

Glucose, also called dextrose, is a moderately sweet monosaccharide with reported relative sweetness values ranging from 50 to 70 at usage level concentrations (Clarke 1996; Godshall 1998). The relative sweetness of glucose is highly dependent on concentration; glucose exhibits an expansion of sweetness with increasing concentration and reaches near-equivalent sweetness to sucrose at concentrations around 50% (Portmann and Birch 1995; Godshall 1998; Godshall 2007). At high concentrations, glucose also presents a bitter side taste (Clarke 1996; Godshall 1998).

The sensory properties of glucose also depend on the form of glucose used. Glucose is commonly consumed as a component of corn syrups, although glucose syrups and crystalline glucose anhydrous and monohydrate are also available (Godshall 2007). The sensory properties of corn syrups are discussed later in this review. The anomeric form of glucose may also affect the perceived sweetness of the monosaccharide; α-D-glucose was been found to be significantly sweeter than β-D-glucose or the equilibrium mixture of the two forms by a highly experienced and sensitive panel (Pangborn and Gee 1961), while a panel of untrained judges found no significant difference between the sweetness of α- and β-D-glucose (Sakaguchi and others 1984). Equilibration of the α- and β-anomers is fairly rapid, with complete equilibration occurring within three hours of solvation at room temperature. The difference in sweetness between the two forms of glucose is also concentration dependent, as the percentage of panelists who identified the α-form as the sweetest sample increases with glucose concentration (Pangborn and Gee 1961).

Corn syrup

For a number of economic and functional reasons, corn syrups have become a major source of sugar in processed foods. Corn syrups are produced from corn starch, and the sweetness and other sensory properties of the corn syrup are largely influenced by the extent to which the starch is broken down into simple carbohydrates. This property is termed the "dextrose equivalent" (DE) and is defined as the dry weight percent of reducing sugars in the syrup (Chinachoti 1995; Godshall 2007). Since mono- and disaccharides are sweeter than polysaccharides, the sweetness of the corn syrup increases with DE (Chinachoti 1995; Godshall 2007). Relative sweetness values for typical corn syrups are listed in Table 2.1 (Kearsley and

others 1980). Corn syrups also have a significant impact on the texture and flavor of foods, adding viscosity, foam stabilization, and humectancy, preventing sugar crystallization, and contributing to browning and flavor development through the Maillard reaction, among other functions (Chinachoti 1995). These properties are also tied to the DE of the corn syrup: viscosity, foam stabilization, and ability to prevent crystallization decrease with increasing DE, while ability to cause browning and flavor development increase with increasing DE (Chinachoti 1995).

Enzymatic isomerization of glucose to fructose in corn syrups produces high-fructose corn syrups with higher relative sweetness and slightly different functional properties (Chinachoti 1995; Godshall 2007; Parker and others 2010). High-fructose corn syrups (HFCS) are classified by the percent fructose of the total dry weight, and the relative sweetness of HFCS increases from around 100 in a 42% HFCS to 120 to 160 in a 90% HFCS (Chinachoti 1995; Clarke 1996; Godshall 2007). The comparable sweetness intensity and "pure sweet" flavor profile make HFCS a popular replacer for sucrose in beverages, baked goods, and confections, among other food applications (Chinachoti 1995; Clarke 1996; Pihlsgard 1997; Parker and others 2010). After sucrose, corn syrup and HFCS are the most versatile and commonly used sweeteners in the United States (Chinachoti 1995; Parker and others 2010).

Sugar alcohols

Sugar alcohols, or polyols, are simply hydrogenated sugars which are less able to be absorbed through the small intestine, contributing to a lower caloric density (Alonso and Setser 1994; Chattopadhyay and others 2014). Other health benefits of sugar alcohols include non-cariogenicity and lower glycemic impact (Ghosh and Sudha 2012). Monosaccharide polyols

(xylitol, sorbitol, mannitol), disaccharide polyols (isomalt, maltitol), and erythritol, a four carbon sugar alcohol, are commercially available (Chattopadhyay and others 2014). The thermal behavior of sugar alcohols is highly dependent on molecular weight; resulting in differences in the thermal behavior of monosaccharide and disaccharide polyols (Cammenga and Zielasko 1996; Yu and others 1998; Borde and Cesàro 2001; Lappalainen and Pitkänen 2006; Ghosh and Sudha 2012). Key thermal properties, glass transition temperature (T_g) and melting temperature (T_m) are shown along with molecular formulas for common sugar alcohols and sucrose in Table 2.3.

Because sugar alcohols are structurally similar to sugars, they can be substituted for sugar at an equal mass ratio and present sweetness and solubility properties in the same range as sucrose, though varying by specific sugar alcohol (Alonso and Setser 1994). Relative sweetness, caloric density, and glycemic index of common sugar alcohol ingredients are compared to the properties of sucrose in Table 2.4. However, sugar alcohols lack reactive keto/aldol functional groups and cannot participate in caramelization or Maillard browning (Alonso and Setser 1994; Godshall 2007; Ghosh and Sudha 2012). Polyols generally crystallize more readily than sucrose, particularly mannitol, which has a very strong tendency to crystallize; though sorbitol can inhibit crystallization of other sugars (Alonso and Setser 1994; Yu and others 1998). Solubility may be a factor of concern for the formulator, as polyols are generally less soluble in water compared to sucrose, with mannitol and isomalt displaying the lowest solubility of the polyols (Ghosh and Sudha 2012). Sugar alcohols vary in hygroscopicity: sorbitol and xylitol are the most hygroscopic, maltitol has low hygroscopicity, and isomalt and mannitol are not hygroscopic (Alonso and Setser 1994). Additionally, sugar alcohols, particularly

monosaccharide polyols, may produce a mouth-cooling effect, which may be desirable or undesirable depending on the context (Alonso and Setser 1994; Ghosh and Sudha 2012).

Synergism in sweetener blends

The sweetness of many sugars and high intensity sweeteners can be increased by creating synergistic blends of sweet compounds (Van Der Heijden and others 1983; Van Tornout and others 1985; Frank and others 1989; Godshall 1995; Colonna and others 2000). Synergistic sweetness is said to occur when the combination of two or more sweet compounds or solutions produce a mixture that is sweeter than the sum of the sweetness of the individual components (Godshall 1995). In general, synergism between sweeteners is highest at low concentrations, small at intermediate concentrations, and can reverse to suppression of sweetness at high concentrations (Frank and others 1989). For example, sucrose and fructose show strong synergism at concentrations around 10%, but only minor synergistic effects at concentrations between 20 to 30% (Partanen 1988; Godshall 1995). Several studies have explored the synergism of sucrose, fructose, and glucose with various high intensity sweeteners, but there is a gap in the literature concerning the synergistic relationship between other mono- and disaccharides and corn syrups (Van Der Heijden and others 1983; Van Tornout and others 1985; Frank and others 1989; Schiffman and others 1995). Corn syrup has been reported to express a suppressive effect on the sweetness of sucrose, but a quantitative analysis of the relationship is not available (Partanen 1988; Godshall 1995).

Schiffman and others (1995) conducted an extensive study that incorporated two sugar alcohols, mannitol and sorbitol, in addition to sugars and high intensity sweeteners in binary mixtures at multiple concentration levels. Sorbitol showed a concentration-dependent

relationship with sucrose, exhibiting synergism at the concentration level corresponding to a 3% sucrose solution, additivity of sweetness at 5%, and suppression of sweetness at 7%. Mannitol showed additivity of sweetness with sucrose at all concentration studied. The percent increase in sweetness of synergistic mixtures of sucrose, glucose, and fructose with six high intensity sweeteners is presented in Table 2.2 (Frank and others 1989).

2.3 Confectionary materials

The history of confectionary preparation and consumption is long and not well documented, but early confectionary goods were likely made from honey and sap, readily available sources of sugar that were components of the prehistoric human diet (Richardson 2002). Several millennia later, refined sugar was available, but expensive; consequently, many varieties of candies were likely developed in the kitchens of the wealthy classes that could afford the ingredients. Confectionary products, as we know them today, proliferated in the 19th and 20th century as the price of refined sugar dropped and industrialized candy manufacturing processes boomed, making the sweet products accessible to a wider population (Erdman 1994; Hartel and Hartel 2014). The business has continued to grow over the last century, as the modern United States' confectionary industry is now a $35 billion industry (National Confectioners Association 2016). Chocolate is the top-selling category of candy, however a plethora of candies are available on the market (Hartel and Hartel 2014; Bartelme 2016). Key categories include hard candies, gummy candies, licorice, tableted candies, chewing gum, fudge, marshmallow, and caramel, to name a few (Edwards 2000; Hartel and Hartel 2014; Bartelme 2016).

Caramel coating systems

Caramel coating systems represent a large class of low moisture, two-phase confections, composed of an amorphous sugar syrup continuous phase with dissolved water-soluble ingredients and dispersed droplets of fats or oils and, in some cases, sugar crystals (Heim 2003; Mendenhall and Hartel 2014). Caramel products have a signature flavor profile; however, texture is often considered the most important attribute of caramels for both the consumer and the manufacturer (Mendenhall and Hartel 2014). The properties of the caramel coating continuous phase are the main drivers of the system texture, and control of moisture content and degree of crystallization are key in controlling the resultant texture of the system (Mendenhall and Hartel 2014). Though the ingredient list of caramel coatings is relatively simple, design and maintenance of caramel texture is considerably complex (Mendenhall and Hartel 2014).

Composition of caramel materials

Carbohydrates dominate the composition of caramel products, and the properties of the caramel system are highly dependent on the ratio of sucrose to corn syrup and the dextrose equivalent (DE) of corn syrup used. Chewy caramels generally have a near 50:50 mix of sucrose and corn syrup, while harder caramels tend to have a greater proportion of sucrose than corn syrup (Flanyak 1991). Higher DE corn syrups result in softer and stickier caramel, while lower DE corn syrups result in harder caramel (Heim 2003; Mendenhall and Hartel 2014). This effect is due to the higher percent composition of large polysaccharides in low DE corn syrups, which act to increase the glass transition temperature (T_g) and the viscosity of the continuous phase (Mendenhall and Hartel 2014). Corn syrup also inhibits recrystallization of sucrose in the system

(Hartel and others 2011). Sucrose, the single most important ingredient in confectionary products, provides an optimal sweetness profile, flavor, bulk, and processing properties that no single substitute can yet replace (Flanyak 1991; Heim 2003; Godshall 2007). In protein-containing caramels, sugars are also responsible for protein aggregation via pH lowering by providing substrates for the Maillard reaction (Weir and others 2016). The state of sugar in caramel systems may be amorphous and/or crystalline, with increasing crystallinity (or "graining") leading to a shorter and less sticky texture (Mendenhall and Hartel 2014). In the amorphous state, sucrose, with reported T_g values ranging from 52 to 74°C, contributes to a desirable glassy texture in caramel coatings (Roos 1995; Vanhal and Blond 1999). Both sucrose and corn syrup also improve product stability by lowering the system water activity (a_w) (Flanyak 1991; Heim 2003). More detailed information on sensory and functional roles of sweeteners in caramel materials is provided in the next section.

Lipids typically make up between 5 and 20% of the formula and play an important role in both the flavor and texture of caramel products (Mendenhall and Hartel 2014). Ideal flavor and mouthfeel are accomplished with butter; however, vegetable oils or fats are more commonly used in commercial production due to lower costs and extended shelf life (Mendenhall and Hartel 2014). In general, incorporation of lipids is reported to reduce overall caramel stickiness (Heim 2003). The influence of lipids on texture also varies by physical state, as solid fats lead to a more firm caramel product, and oils lead to a softer and potentially stickier texture (Mendenhall and Hartel 2014). Optimally, lipids enhance caramel flavor and texture, but oxidative rancidity and phase separation can also occur over time or with improper handling (Heim 2003).

Water makes up around 8 to 12% (wet basis, % wb) of soft caramel products and only 1 to 3% (wb) of caramel coating type materials, but plays a significant role in graining behavior of caramels, hardness, and stability (Heim 2003; Mendenhall and Hartel 2014). Water acts as a plasticizer in caramel systems, reducing the system T_g and pushing the material towards the rubbery state with increasing moisture content (Roos 1995). The depression of T_g with the addition of water is also to be expected due to the very low theoretical T_g of water (-135°C) (Mendenhall and Hartel 2014). Moisture content is a primary factor used to control final product properties, and especially texture, through change of final cook or processing temperature. Traditional caramels are heated to 240-270°F, while caramel coatings and hard candies are heated to 280-330°F (Flanyak 1991).

Caramel sensory properties contributed by sugars

As discussed in the previous section on carbohydrates, sugars play a vital role in producing many of the characteristic properties of caramel materials. Replacement of sugar within caramel or other confectionary materials has the potential to significantly alter the sensory profile of the products, particularly influencing aroma and flavor, color, and texture attributes. The impact of sugar replacement on these properties must be carefully considered in order for reduced-sugar prototypes to succeed.

Flavor properties characteristic of caramel are produced by reactions of the sugar, caramelization and/or the Maillard reaction, in the system. At high temperatures, or at moderate temperatures for longer times, caramelization of sucrose results in generation of flavors and colors ranging from caramel-like, vanilla, and light-brown, to bitter, burnt, and dark

brown to black (Monte and Maga 1982; Godshall 1998; Jiang and others 2008; Lee, Leonard C. Thomas, and others 2011). Caramelization is generally desirable and produces pleasant aromas, but can result in undesirable sensory attributes as the degree of caramelization increases (Monte and Maga 1982; Godshall 1998). In protein-containing caramel formulations, sucrose break-down products can also serve as substrates in the Maillard reaction, a complex system of chemical reactions of proteins with reducing sugars to produce a vast array of flavor volatiles, including the caramel-like furans, Strecker aldehydes, licorice-like cyclopentenes, and nutty pyrazines, among others (Monte and Maga 1982; Pihlsgard 1997; Colonna and others 2000).

Color characteristics of caramels are produced through the polymerization of Maillard reaction products, as well products of the caramelization of sugars or carbohydrates, to form melanoidins, which impart a brown color (Heim 2003; Paravisini and others 2012; Clemens and others 2016).

Texture attributes of caramel products are heavily influenced by the ratio of sugars to larger carbohydrate compounds, though moisture, lipids, and processing parameters also play a role (Flanyak 1991; Hartel and others 2011). Caramel texture can range from hard and brittle to soft and sticky, though previous research shows a consumer preference for crunchy texture in caramel coated popcorn products (Beck and others 2002). Stickiness in caramel materials also causes severe problems in manufacturing, as even low amounts of adhesion can produce significant technical hurdles (Mendenhall and Hartel 2014). In general, the physical property of stickiness is defined as a combination of tack (bonding between material and surface) and adhesion (combined adhesive and cohesive forces). However, this property is difficult to

measure in food materials because the design and implementation of stickiness measurements is complex and, more significantly, stickiness perception is dynamic and varies by person and product (Mendenhall and Hartel 2014).

2.4 Methods to measure sensory properties of confectionary materials

Sensory analyses provide unique benefits and challenges. By directly measuring human responses to foods, sensory testing can provide the most accurate data on human perception of food properties (Lawless and Heymann 2010). Though informal sensory evaluations are as old as human history, development of most formalized sensory methods dates from the mid-twentieth century to present day (Meilgaard and others 1991; Lawless and Heymann 2010). Most sensory protocols can still be described by one of three core categories of sensory test methods: discrimination, descriptive, and affective tests (Lawless and Heymann 2010). Sensory methods differ in both the type of data collected and the appropriate type of panelist to utilize; an effective sensory test will carefully match the protocol and participants to goals of the study (Meilgaard and others 1991). In analytical tests, which include discrimination and descriptive methods, humans are used as analytical instruments to provide assessments of the perceptibility of product differences or the characterization of product attributes (Lawless and Heymann 2010). In contrast, affective tests utilize novice, consumer panelists and seek subjective evaluations of products (Lawless and Heymann 2010).

Expanding on these core methodologies, additional methods which provide specific advantages are steadily being added to the sensory toolbox. Advantages of alternative methods include the ability to probe additional dimensions of sensory properties, as in temporal test

methods (Pineau, Cordelle, and Schlich 2003; Lawless and Heymann 2010), to collect the same type of data more efficiently, as in flash descriptive profiling methods (Dehlholm and others 2012), or to enable untrained panelists to participate descriptive-style tests, as in consumer profiling methods like check-all-that-apply (CATA) (Lancaster and Foley 2007; Dooley and others 2010). Recent years have seen a proliferation of publications involving consumer profiling of products or comparison of sensory profiles generated by trained and novice panelists (Gómez and others 1998; Hersleth and others 2005; Dooley and others 2010; Worch and others 2010; Ares and others 2015; Bruzzone and others 2015; Ferreira and others 2016; Galmarini and others 2016). This trend may reflect an interest in testing the congruency between trained panelist evaluations and consumer perceptions of product attributes, a drive to increase the time-efficiency of sensory data collection, or a gradual shift in the field towards a more consumer-focused approach (ten Kleij and Musters 2003; Symoneaux and others 2012; Varela and Ares 2012; Ares 2015; Fonseca and others 2016; Xue and others 2016). An overview of selected traditional novel sensory test methods is illustrated in Figure 2.3.

A broad range of traditional and novel analytical methods have been utilized to measure the sensory properties of confectionary materials, including descriptive analysis, CATA, rate-all-that-apply (RATA), time-intensity (TI), and temporal dominance of sensation (TDS) (Seaman and others 1997; Steiner and others 2003; Schober and Peterson 2004; Ares, Deliza, and others 2010; Saint-eve and others 2011; Giacalone and Ingholt 2016; Wagoner and others 2016). A brief introduction to a selection of sensory methods that can be utilized to measure sensory properties or characterize the sensory profile of confectionary properties follows.

Analytical sensory methods

Descriptive sensory analysis

Descriptive sensory analysis is the benchmark method for the description and quantification of sensory properties of a product (Murray and others 2001). A family of related techniques that share the same basic tenants includes, in approximate order of development, the Flavour Profile Method (FPM), the Texture Profile Method (TPM), Quantitative Descriptive Analysis (QDA®), the Quantitative Flavour Profiling Technique (QFP), the Spectrum™ method (Caircross and Sjostrom 1950; Szczesniak 1963; Stone and others 1974; Meilgaard and others 1991; Stampanoni 1994; Murray and others 2001). Generic descriptive analyses, which employ a flexible blend of methodological elements from other descriptive methods, are now common and will be used to explain the common features of descriptive analyses (Murray and others 2001; Lawless and Heymann 2010).

Descriptive analysis panels are typically composed of between 8 and 12 screened and highly trained panelists and one panel leader who leads training and facilitates sample evaluation (Meilgaard and others 1991; Murray and others 2001; Lawless and Heymann 2010). A wide variety of human senses are often utilized in isolation to assess specific product properties (i.e., visual attributes assessed via sight, aroma attributes assessed via smell, tactile attributes assessed via touch by the hand or in mouth) (Meilgaard and others 1991; Pereira and others 2002; Lawless and Heymann 2010). Depending on the goals of the study, panelists may assess all modalities of sensation to generate a complete sensory profile, or they may focus their evaluation on only a subset of product characteristics (Meilgaard and others 1991; Lawless and Heymann 2010).

Panelist training is quite extensive and generally involves introduction to the methodology (for new panelists), generation of terms to describe relevant sensory attributes, selection of references and definitions to standardize the understanding of selected attributes, scaling of references, and practice evaluation of products (Stone and others 1974; Meilgaard and others 1991; Lawless and Heymann 2010). Sample evaluation should be conducted in a highly-controlled environment to minimize extraneous sources of bias or variation (Meilgaard and others 1991). The ultimate data output of descriptive analysis are attribute intensity scores, which may be rated on either a line or categorical scale (Meilgaard and others 1991; Lawless and Heymann 2010). Data from descriptive panels may be used to produce a sensory fingerprint for a product, compare the sensory profile of multiple products, or identify drivers of product liking by consumers (Murray and others 2001; Lawless and Heymann 2010).

Novel analytical sensory methods

Napping

The Napping method represents one of many rapid descriptive methods recently developed or accepted in the field of sensory science (Dehlholm and others 2012; Varela and Ares 2012). The Napping method, first published by Pagès (2003), may be considered a rebranding of the projective mapping method (Risvik and others 1994). Like projective mapping, Napping provides quantitative insights into the perceived relative similarity of products in a set by asking panelists to position samples on a two-dimensional plane based on their own criteria, such that similar samples are close together and dissimilar samples are far apart (Risvik and others 1994; Pagès 2005; Lawless and Heymann 2010). In order to explain the sensory attributes driving perceived product differences, Napping is frequently paired with

Ultra Flash Profiling (UFP) (Pagès 2005; Dehlholm and others 2012). In Napping-UFP studies, panelists are instructed to write in descriptive terms that describe the samples or sample clusters after positioning the samples in the set across the two-dimensional workspace provided (Pagès 2003; Dehlholm and others 2012). Multiple factor analysis can be applied to the quantitative and qualitative data sets, producing a factor map that resembles a principal component analysis (PCA) biplot typically produced to summarize traditional descriptive sensory data (Pagès 2005; Lawless and Heymann 2010; Varela and Ares 2012).

Napping-UFP and projective mapping methods have been implemented in panels with a wide range of training or expertise in evaluating the product category; it can be an appropriate method for both novice or consumer panelists and trained or expert panelists (Pagès 2003; Pagès 2005; Lawless and Heymann 2010; Varela and Ares 2012; Reinbach and others 2014; Liu and others 2016). However, the number of panelists recommended to attain a stable sample configuration is dependent on the degree of expertise of the panelists. As few as eight panelists with a high degree of expertise have comprised a Napping panel (Pagès 2005), while between 15 and 50 panelists are recommended for consumer Napping or projective mapping studies (Albert and others 2011; Varela and Ares 2012; Vidal and others 2014).

Check-all-that-apply

Check-all-that-apply (CATA) type questions have long been a fixture of surveys or questionnaires, but only recently have CATA questions been applied as a descriptive sensory method for efficient characterization and comparison of the sensory profile of products (Rasinski and others 1994; Lancaster and Foley 2007; Varela and Ares 2012; Reinbach and others 2014). A CATA test prompts panelists to select all sensory attributes perceived in a

sample from a list of possible attributes, which have been generated prior to the test (Lancaster and Foley 2007; Valentin and others 2012). The method has gained popularity as a rapid descriptive technique to the simplicity of the task, which makes the method appropriate for untrained or consumer evaluators (Valentin and others 2012; Reinbach and others 2014).

Insights into the intensity or importance of attributes are limited due to the binary nature of the dataset (i.e., an attribute either is or is not selected by each panelist for a given sample); however, statistical methods have been developed to assess differences in the frequency of attribute selection between products (Lancaster and Foley 2007; Dooley and others 2010; Valentin and others 2012). Common methods of data analysis include Cochran's Q test for the determination of significant differences in the application of sensory terms to the sample set and Correspondence Analysis (CA) or Multiple CA (MCA) for the comparison of product profiles within a two-dimensional sensory space (Lancaster and Foley 2007; Valentin and others 2012; Jaeger and others 2014).

Sensory profiling via CATA is currently a hot research topic, generating a proliferation of publications on both utilization of the method (Ares, Barreiro, and others 2010; Dooley and others 2010; Ares and others 2015; Jaeger and others 2015) and on the assessment of potential weakness and biases of the method (Ares and others 2013; Jaeger and others 2013; Ares, Antúnez, and others 2014; Jaeger and Ares 2014). Interest in the method has also led to the recent development of two methodological extensions: Rate-all-that-apply (RATA), which adds an intensity or applicability component to traditional CATA questions (Ng and others 2013; Ares, Bruzzone, and others 2014), and Temporal CATA (TCATA), which adds a temporal

dimension by asking panelists to select and deselect terms as they present and fade across the evaluation period (Castura and others 2016).

Temporal dominance of sensation

Temporal dominance of sensation (TDS) was introduced by Pineau and others (2003) as an efficient method for the measurement of temporal sensory profile (Pineau, Cordelle, Imbert, and others 2003; Lawless and Heymann 2010). In contrast to Time Intensity (TI), in which the intensity of selected attributes are continuously evaluated one attribute at a time, TDS is designed for simultaneous evaluation of multiple attributes (Labbe and others 2009; Lawless and Heymann 2010). In a TDS test, panelists are instructed to select from an attribute list or grid the attribute that dominates their attention at a given moment during the evaluation period (Labbe and others 2009). Attributes are considered to be dominant from the moment of selection until the selection of the next dominant attribute. Because panelists must select the dominant attribute from a list of terms as close as possible to the moment in which the attribute becomes dominant, the number of attributes which can be included in a TDS study is naturally limited to 10 or fewer terms so that the list of terms to choose from does not become unwieldy (Pineau and others 2012).

In early reported uses of the TDS method, panelists were also asked to rate the intensity of attributes immediately after selection as the dominant attribute, but this rating task adds significantly to the burden on panelists and is now often omitted from TDS tests (Labbe and others 2009; Lawless and Heymann 2010; Pineau and others 2012; Di Monaco and others 2014). Additionally, data regarding the duration of dominance and total percent dominance (i.e., panelist agreement about which is the dominant attribute) have proven to be sufficient in

characterizing and comparing temporal profiles of products (Dinnella and others 2013; Di Monaco and others 2014). Familiarization with the method must precede effective TDS testing; however, panelists of varying degrees of training or expertise in evaluation of the product category may be utilized (Pineau and others 2012; Rodrigues and others 2016). It is recommended to collect at least 30 evaluations per product, and published panel sizes have ranged from 7 to 44 panelist, with 16 panelists emerging as the mode (Pineau and others 2012). Common methods of sensory data analysis have been adapted to analyze TDS data and embedded into the TimeSens software package, including analysis of variance (ANOVA), canonical variates analysis (CVA), and PCA (Visalli and others 2011; Dinnella and others 2013). A new statistical method, trajectory PCA, which tracks duration of dominance across subsets of mastication time, has also been developed for visualization of TDS-derived temporal profiles (Visalli and others 2011).

2.5 Modeling of sensory properties

While sensory testing provides the truest insights into human perceptions, predictive models can provide reliable information about sensory properties without the time and expense required to collect data from human subjects (Lawless and Heymann 2010). By utilizing relationships between physical or formulation variables and relevant sensory properties, well-constructed models can enable powerful prediction of sensory properties and rapid screening of products or prototypes. Typically, models have been used to predict objective sensory properties, including color, aroma, taste, mouthfeel, and texture properties of foods and beverages. However, models have also been constructed to predict consumer acceptance, as in

the work by Cruz and others (2013), which proposes a model to estimate consumer liking based on whey content in probiotic dairy beverages.

The type of data utilized to model sensory properties varies widely by the product and properties of interest, but common categories include mechanical or rheological testing (Meullenet and others 1997; Saint-Eve and others 2006; Salvador and others 2009), infrared spectroscopy (Andrés and others 2007; Fagan and others 2007), image analysis (Basset and others 2000; Martens and Thybo 2000; Zheng and others 2006; Fongaro and Kvaal 2013). Sensory properties modeled also span a broad range, including color (Thai and Shewfelt 1991), aroma (Andriot and others 2000; Piagentini and others 2005), and texture (Meullenet and others 1997; Martens and Thybo 2000; Saint-Eve and others 2006; Salvador and others 2009; Fongaro and Kvaal 2013).

Sensory properties of foods are often modeled based on measurable properties of the final food material, as in Salvador and others' prediction of potato chip texture from mechanical and acoustic fracture parameters of the chips (2009). Alternatively, properties of a final food product can be forecasted based on properties of a raw material prior to processing or cooking. The benefit of this type of model is evident in applications like the evaluation of meat quality from properties of the muscle tissue (Basset and others 2000; Arvanitoyannis and van Houwelingen-Koukaliaroglou 2003; Andrés and others 2007), in which the properties of the food product as sold differ from the properties of the product when consumed. Enhancing the predictive value of these models by shifting inputs and predictions earlier in the food production pipeline, this approach has been extended to the modeling of sensory attributes

from measurable properties of component ingredients. The value of these advanced predictive models is demonstrated in the work of Vlassides and others (2001) on the prediction of wine characteristics from properties of grapes. If well calibrated, these models can empower food producers to control and improve quality (Vlassides and others 2001; Kulmyrzaev and others 2005). Further discussion of several instrumental approaches for characterization or modeling of food texture follows.

Texture profile analysis

Texture Profile Analysis (TPA) was developed as an instrumental method to approximate sensory texture properties and has demonstrated mixed success in approximating texture attributes as perceived by human evaluators (Breene 1975; Bourne 1978; Szczesniak 2002). Through measurement of the forces caused by customizable mechanical interactions of a probe with a food material, Texture Analysis, and TPA specifically, aim to quantify the forces at play in mastication and texture perception (Breene 1975; Bourne 1978). TPA measurements of hardness generally correspond strongly to sensory perception of hardness (Szczesniak 2002). More complex textural properties, such as stickiness or creaminess, are often difficult to predict instrumentally, although success is possible through careful optimization of method parameters (Szczesniak 2002). For example, probe tack force has been found to correlate significantly with sensory stickiness in caramel systems (Steiner and others 2003) and numerous significant correlations were found between TPA parameters and sensory evaluation of firmness, chewiness, and crumbliness in cereal bars (Kim and others 2009).

Moisture content

The moisture content of a food material is a single compositional variable with a large impact on food properties and stability, and particularly food texture (Arvanitoyannis and van Houwelingen-Koukaliaroglou 2003; Ergun and others 2010). Correlations between moisture content and texture have been documented for food systems including cereal bars (Kim and others 2009) and model cheeses (Pereira and others 2002). Moisture content is also a variable of interest to study in relation to texture control because final moisture content can be fairly easily altered through formula or processing changes (Foegeding and Steiner 2002; Ergun and others 2010).

Water activity

Water activity (a_w) is a measure of the partial vapor pressure of material compared to the partial vapor pressure of pure water at the same temperature and pressure (Labuza 1980). a_w is a commonly utilized parameter in food applications due to the well-understood relationships between a_w and the microbiological, enzymatic, and chemical stability of a food (Labuza 1980; Labuza and Fu 1993). The relationship between a_w and texture is implied through reported trends or categories of products and product textures along the a_w spectrum, though a_w is not a frequently utilized metric for explaining texture (Schmidt 2004). In addition to associations between a_w ranges and textural properties, water activity gradients can drive textural changes during storage in multi-component food products (Labuza and Hyman 1998). More anecdotal observations have been formalized through publication of direct correlations between sensory texture attributes, including crispness (Katz and Labuza 1981) and strong, but

not statistically significant correlations to firmness, chewiness, and crumbliness (Kim and others 2009).

Differential scanning calorimetry

The application of a food materials science approach to measurement and understand of food properties was championed by Levine and Slade (1986; 1991). In the review article "Beyond water activity: Recent advances based on an alternative approach to the assessment of food quality and safety" (Slade and others 1991), Levine and Slade articulate the relevance of thermal properties of foods, often measured via differential scanning calorimetry (DSC), for characterization of food materials and prediction of food material properties. Through DSC analysis, the physical state of a solid material (crystalline or amorphous) and the temperature at which phase and state changes occur can be measured. DSC is often utilized to quantify the degree of crystallization, which has a strong bearing on the resultant textural attributes in confectionary products (Hartel and others 2011; Mendenhall and Hartel 2014; Miller and Hartel 2015).

The temperature at which materials transition from a glassy to rubbery amorphous state, termed the glass transition temperature (T_g), relates strongly to food texture and stability (Slade and others 1993). The relevance of Tg to stickiness has been studied extensively from a processing perspective (Roos 2010). Roos and Karel (1991) detailed the onset of a "sticky point" in relation to the T_g of carbohydrate materials at various moisture contents. This work was later extended by Chuy and Labuza (1994) and Silalai and Roos (2010) to the study of caking and mechanical stickiness in milk powders at various a_w values. The glass transition has an intuitive relationship to texture in amorphous food materials, as the separation between sample glass

transition temperature and the temperature at which the sample is consumed or evaluated for sensory texture properties (i.e., room temperature, oral temperature) directly relates to the relative glassy or rubbery nature of the sample. Samples evaluated below their T_g can be expected to display textural properties of a glass, while samples evaluated above their T_g can be expected to display textural properties of a rubber. Correlations between T_g and sensory measures of texture have shown promise; T_g has been found to correlate positively with hardness and crispness, and negatively with adhesiveness (Martinez and Chiralt 1995; Le Meste and others 1996; Huang and Hsieh 2005; Payne and Labuza 2005).

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2.7 Figures and tables

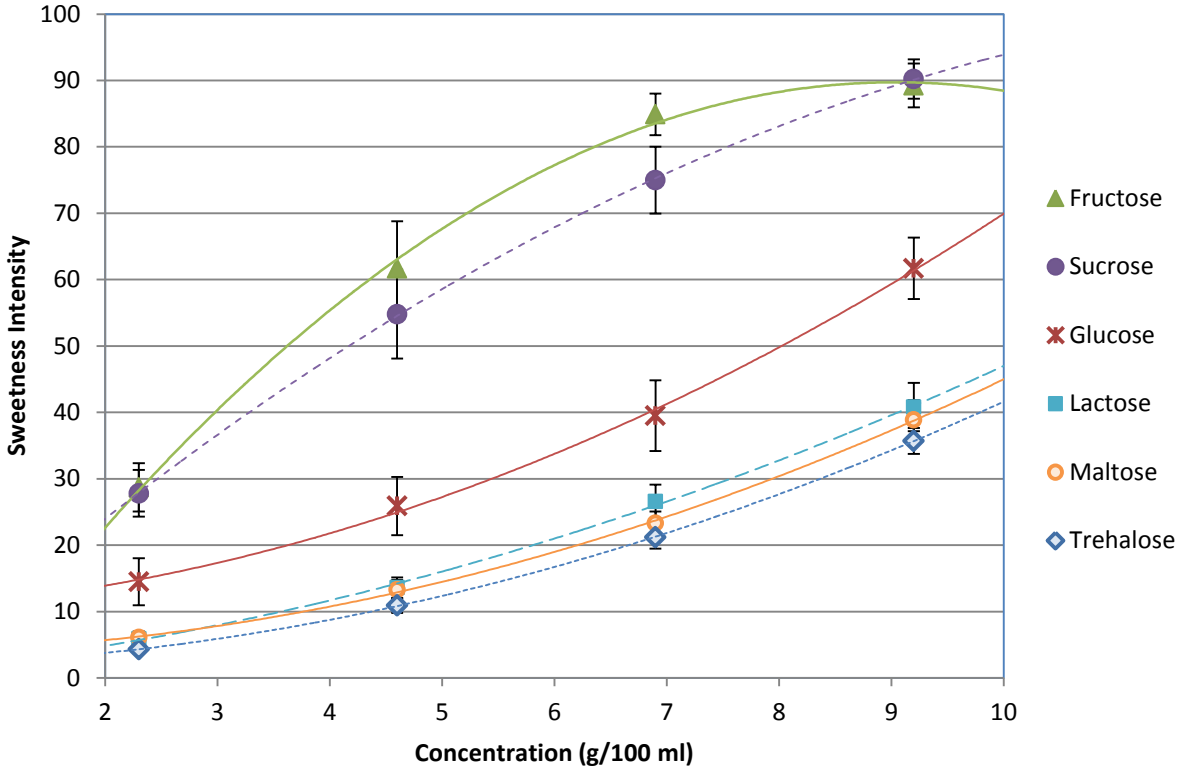

Figure 2.1. Intensity of sweetness sensation as a function of concentration for fructose, sucrose, glucose, lactose, maltose, and trehalose. Fructose and sucrose exhibit compression of sweetness with increasing concentration, while glucose, lactose, maltose, and trehalose exhibit expansion of sweetness with increasing concentration (Portmann and Birch 1995).

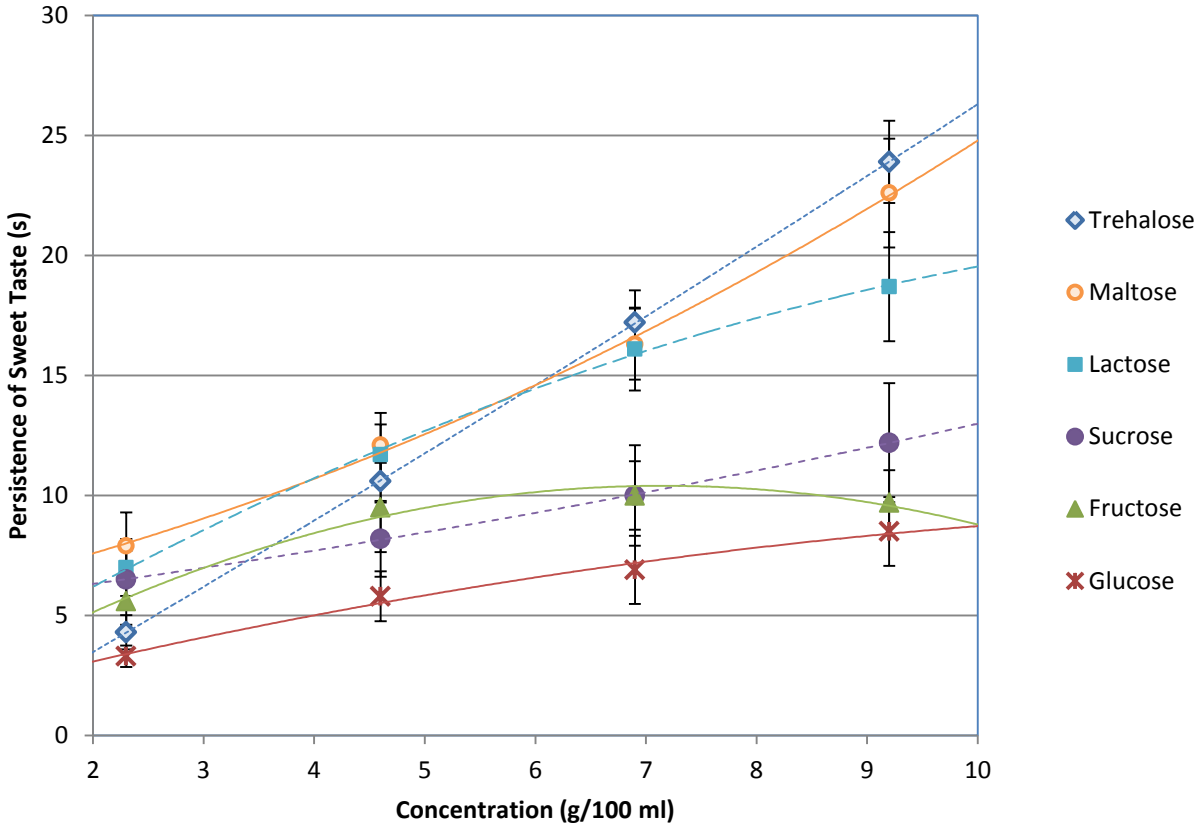

Figure 2.2. Persistence of sweetness sensation in seconds as a function of concentration for fructose, sucrose, glucose, lactose, maltose, and trehalose (Portmann and Birch 1995).

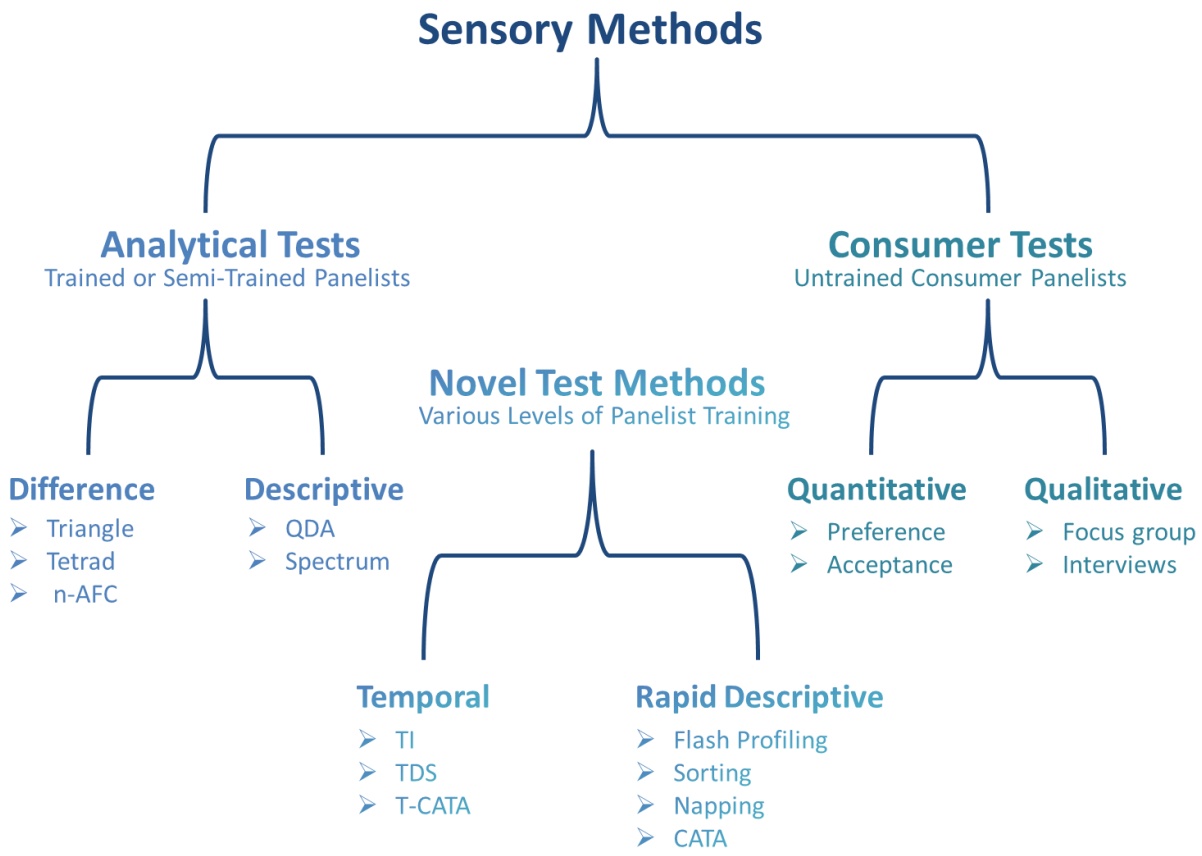

Figure 2.3. A schematic of many commonly utilized sensory test methods, categorized by test type and degree of required panelist training.

Table 2.1. Relative sweetness values for common sugars, corn syrup at various dextrose equivalent (DE) values, and high fructose corn syrup at various fructose percentages, as a percent of the sweetness of sucrose at equal concentration (Kearsley and others 1980; Clarke 1996; Godshall 1998; Colonna and others 2000; Higashiyama 2002; Godshall 2007).

Sugar		**Relative Sweetness**
Sucrose		**100**
Fructose		115-180
Glucose		50-70
Galactose		54
Lactose		15-40
Maltose		30-50
Trehalose		45
Corn syrup, various DE	15 DE	14
	18 DE	18
	25 DE	21
	37 DE	27
	42 DE	38
	43 DE	30
	52 DE	43
	64 DE	58
	78 DE	63
	86 DE	58
High fructose corn syrup, various fructose %	90%	120-160
	55%	>100
	42%	100

Table 2.2. Percent increase in sweetness as a result of synergistic sweetener blend for sucrose, fructose, glucose, and several common high intensity sweeteners (Frank and others 1989).

Sugar	Sucrose	Fructose	Glucose	Aspartame	Saccharin	Acesulfame K	Cyclamate	Xylitol	Stevioside
Sucrose		8	2	11	19	14	15	18	7
Fructose	8		-1	7	NR	11	4	3	-11
Glucose	2	-1		9	NR	11	13	-1	-12

NR = not reported; negative values indicate a suppression of sweetness occurs in the blend instead of synergism

Table 2.3. Molecular formula, published glass transition temperature (T_g) midpoint values and melting temperature (T_m) onset values, and the literature sources of thermal data for sucrose and commonly utilized sugar alcohols: isomalt, lactitol, maltitol, mannitol, sorbitol, xylitol, and erythritol.

Ingredient	Molecular Formula	T_g midpoint (°C)	T_m onset (°C)	Literature sources
Sucrose	**$C_{12}H_{22}O_{11}$**	**70**	**151**	(Lee, Leonard C. Thomas, and others 2011; Lee, Leonard C Thomas, and others 2011)
Isomalt**	$C_{12}H_{24}O_{11}$	60	142	(Cammenga and Zielasko 1996; Borde and Cesàro 2001)
Lactitol	$C_{12}H_{24}O_{11}$	65	146	(Mcfetridge and others 2004)
Maltitol	$C_{12}H_{24}O_{11}$	48 to 50	147 to 150	(Bustin and Descamps 1999; Hurtta and Pitkänen 2004; Lappalainen and Pitkänen 2006)
Mannitol*	$C_6H_{14}O_6$	13	158 to 167	(Yu and others 1998)
Sorbitol	$C_6H_{14}O_6$	-2	93 to 112	(Yu and others 1998; Ghosh and Sudha 2012)
Xylitol	$C_5H_{12}O_5$	-23	95	(Carpentier and others 2003)
Erythritol	$C_4H_{10}O_4$	-45 onset	118	(Talja and Roos 2001)

*poylmorphs; **mixture of disaccharides

Table 2.4. Published relative sweetness values, caloric density (Cal/g), and glycemic index for sucrose and commonly utilized sugar alcohols: isomalt, lactitol, maltitol, mannitol, sorbitol, xylitol, and erythritol. Values in this table are reproduced from Godshall 2007 and Chattopadhyay and others 2014.

Ingredient	Relative Sweetness	Caloric Density (Cal/g)	Glycemic Index
Sucrose	**1.00**	**4.0**	**61 to 65**
Isomalt	0.45 to 0.65	2.0	2
Lactitol	0.35 to 0.40	2.4	6
Maltitol	0.50 to 0.90	3.0	35 to 52
Mannitol	0.50 to 0.72	1.6	0
Sorbitol	0.60	2.6	9
Xylitol	1.00	3.0	7 to 13
Erythritol	0.70	0.2	0

Chapter 3: Napping-Ultra Flash Profile as a tool for category identification and subsequent model system formulation of caramel corn products

3.1 Abstract

In a novel approach to formulation, the flash descriptive profiling technique Napping-Ultra Flash Profile (Napping-UFP) was used to characterize a wide range of commercial caramel corn products. The objectives were to identify product categories, develop model systems based on product categories, and correlate analytical parameters with sensory terms generated through the Napping-UFP exercise. In one 2 h session, 12 panelists participated in four Napping-UFP exercises, describing and grouping, on a 43x56 cm paper sheet, 12 commercial caramel corn samples by degree of similarity, globally and in terms of aroma-by-mouth, texture, and taste. The coordinates of each sample's placement on the paper sheet and descriptive terms generated by the panelists were used to conduct Multiple Factor Analysis (MFA) and hierarchical clustering of the samples. Strong trends in the clustering of samples across the four Napping-UFP exercises resulted in the determination of three overarching types of commercial caramel corn: "small-scale dark" (typified by burnt, rich caramel corn), "large-scale light" (typified by light and buttery caramel corn), and "large-scale dark" (typified by sweet and molasses-like caramel corn). Representative samples that best exemplified the properties of each category were used as guides in the formulation of three model systems that represent the spread of commercial caramel corn products. Analytical testing of the commercial products, including a_w measurement, moisture content determination, and thermal characterization via differential scanning calorimetry, were conducted and results related to sensory descriptors using Pearson's correlation.

3.2 Introduction

Napping emerged in 2003 as a new method in a string of rapid alternatives to conventional descriptive sensory test methods (Pagès 2003; Dehlholm and others 2012). These rapid descriptive methods show great promise as more efficient, time and cost-effective precursors or replacements to traditional descriptive analysis procedures and their potential applications are still being explored. Napping bears closest resemblance to its predecessor, Projective Mapping, an amalgamation of sorting and Flash Profile methods (Risvik and others 1994; Dehlholm and other 2012; Pagès 2003).

Deriving its name from the French word for tablecloth, Napping is based on the simple arrangement of samples on a tablecloth or sheet of paper (Pagès 2003). Untrained panelists are presented with a complete sample set and instructed to arrange the samples such that proximity of the samples is directly related to perceived similarity of the samples by whatever criteria the panelist finds logical.

A newer variant of this method, termed Partial Napping, restricts the criteria used for placement of samples to a specific sensory modality (Dehlholm and others 2012). In contrast, Global Napping, or Napping as originally designed, encourages panelists to use the complete sensory profile of samples in their arrangement of the group (Pagès 2003). Due to the lack of required training and the simplicity of the experimental design, a single Napping exercise is typically completed in half an hour or less (Dehlholm and others 2012).

Napping is customarily paired with Ultra-Flash Profiling (UFP), termed herein as Napping-UFP. In this hybrid method, panelists are instructed to jot down some sensory descriptors used in their differentiation of samples and groups of samples by the marked and labeled placement

of samples on the paper mat (Pagès 2005; Dehlholm and others 2012). In this way, quantitative and qualitative data are simultaneously and quickly collected. Coordinates of the samples on the mat and frequencies for sensory terms generated are tabulated and subjected to Multiple Factor Analysis (MFA) (Escofier and Pagès 1994; Perrin and others 2008; Pagès 2003; Pagès 2005; Lê and others 2008). Sensory descriptors are typically not used as active variables, but are very helpful in explaining the averaged positioning of samples in MFA graphical output (Escofier and Pagès 1994; Pagès 2005; Le and others 2008).

The Napping-UFP method is typically used as a convenient way to identify major sensory differences that distinguish samples in a set and to provide a preliminary sensory characterization of a sample set. A diverse range of samples have been analyzed with this method, including alcoholic beverages, liver pâtés, and green teas, among others (Pagès 2003; Pagès 2005; Giacalone and others 2013; Louw and others 2013; Dehlholm and others 2012; Kim and others 2013). Comparative studies have shown that Napping provides a good value of meaningful results for the time required, making it an appropriate choice when a high degree of precision and power is not required (Dehlholm and others 2012; Valentin and others 2012). The first aim of this research was to implement the Napping-UFP method and hierarchical clustering analysis as a means of rapid categorization and characterization of the spread of a product category. Caramel corn was selected as the target product category due to the scarcity of published research on caramel corns and the interesting thermal properties of caramel coating systems. We hypothesized that trends in panelist clustering and description of caramel corn products could be used to characterize key categories of commercially available products. The second aim was to use information gleaned from the Napping-UFP exercise to direct the

formulation of caramel coating model systems based on the characterization and members of the caramel corn subcategories generated. In this aim, we hypothesized that formulation of commercially relevant caramel coating model systems could be achieved using Napping-UFP derived caramel corn categories as guides. The final aim was to validate UFP data through meaningful correlation of UFP panelist-generated sensory descriptors with relevant measured thermal and physical properties of the products surveyed. We hypothesized that important sensory properties described by panelists during the UFP exercise could be supported by and correlated to commonly measured thermal and physical properties of the samples.

3.3 Materials and methods

Caramel corn sample selection

A representative sample of caramel corns was selected to encompass the range of commercially available products. Eight mass-produced, commercial products ("large-scale"; coded with numbers 1-8) were chosen, along with four fresh, hand-made caramel corn products ("small-scale"; coded with numbers 9-12). Large-scale samples were purchased in local stores, while small-scale products were ordered from vendors. Two products with nutrient claims, one fat free product (sample number 7) and one sugar free product (sample number 8), were also selected for evaluation.

Napping procedure

Twelve panelists were recruited (2 male, 10 female; ages 22 to 50) to participate in the Napping exercise. The Global and Partial Napping procedures were paired with Ultra-Flash Profiling (UFP) as described by Dehlholm and others (2012). The group of panelists, which met for one 2 h session, was introduced to the Napping method and presented with a 43 cm by 56

cm sheet of white paper and 12 caramel corn samples in 140 ml cups, labeled with random 3-digit codes. Panelists tasted and expectorated all samples. Between samples, panelists rinsed with carbonated water, warm water, and room temperature water. The panelists were instructed to arrange the samples on the sheet of paper such that the most similar samples were closest together and the most different samples were farthest apart. This exercise was conducted first for the overall sensory impression of the products (Global Napping), and then repeated for texture, aroma-by-mouth, and taste attributes individually (Partial Napping).

After each Napping exercise, panelists marked the position of each sample on the Napping paper with an X and labeled the X with the sample code. For the UFP portion of the test, panelists labelled sample positions with some descriptive phrases used to characterize the sensory attributes of the sample. An example Napping paper with coordinates and descriptors generated by one panelist during the Napping exercise is shown in Figure 3.1. The X and Y coordinates of each sample on each Napping paper were measured to the nearest millimeter from the lower left corner of the sheet. Qualitative terms were recorded for each sample and exercise.

Analytical testing

Water activity (a_w) was measured for each product at 25 °C using an AquaLab 4TE instrument (Decagon Devices, Inc., Pullman, WA, U.S.A.). Caramel corn samples were cut into small pieces to increase sample surface area and facilitate equilibration. Measurements were collected twice, once immediately after purchase (0 month) and once after a month of storage

at ambient conditions in the resealed original package (1 month). All measurements were made in duplicate.

Moisture content of caramel corn samples was measured using vacuum oven drying and weight loss calculation. Caramel corn samples were ground (particle size 1-3mm in diameter) with a 10 cm ceramic mortar and pestle and weighed out into dry 115 ml aluminum pans (Handi-Foil of America, Inc., Wheeling, IL, U.S.A.). The placement of the pans in the Equatherm Vacuum Oven (Curtin Matheson Scientific, Inc., Houston, TX, U.S.A.) was randomized in order to minimize the effect of any temperature gradient within the oven. Samples were held under vacuum at 60 °C for 24 h. Measurements were made in duplicate for each sample. Weight loss was measured and average moisture content calculated for each sample. In order to track changes in moisture content during storage, moisture content measurements were collected twice, once immediately after purchase (0 month) and once after a month of storage at 22 °C in the resealed original package (1 month).

Differential scanning calorimetry (DSC) was used to obtain the thermal characteristics of the caramel coating systems. All testing was conducted using a DSC Q2000 autosampler (TA Instruments, New Castle, DE, U.S.A.) with a refrigerated cooling system (RCS 90). Prior to testing, the DSC Q2000 was calibrated for temperature and enthalpy using indium as a standard (known melting temperature: $T_{m\ onset}$ of 156.6 °C; known enthalpy: ΔH of 28.71 J/g). All sample testing and calibrations were carried out using a purge gas of dry nitrogen at a flow rate of 50 mL/min and hermetically sealed aluminum Tzero pans and lids (TA Instruments, New Castle, DE, U.S.A.).

Caramel coating was flaked off each product to isolate the caramel coating from the popcorn. Caramel coating samples (~5 to 10 mg) were equilibrated at -40 °C, heated at a rate of 10 °C/minute to 100 °C, rapidly cooled to -40 °C, and then heated at a rate of 10 °C/minute to 200 °C. An additional testing method, in which samples were equilibrated at -40 °C and then heated at a rate of 10 °C/minute to 200 °C, was also used for selected caramel coating samples. All DSC scans were analyzed using Universal Analysis software (Version 4.4A, TA Instruments, New Castle, DE, U.S.A.) to determine parameters associated with the glass transition (T_g onset, T_g midpoint, T_g endpoint), physical aging (ΔH_{aging}), and melting (T_m onset, T_m midpoint, ΔH_m) of the coating system upon heating and the crystallization of butter ($T_{c\text{-}butter}$ onset, $T_{c\text{-}butter}$ midpoint, $\Delta H_{c\text{-}butter}$) upon cooling. Parameters corresponding to the glass transition were collected using manual tangent selection with the step midpoint at half height, and parameters corresponding to melting and crystallization of butter peaks were collected using the sigmoidal peak integration function.

Caramel preparation

Ingredient lists for selected caramel corn samples (Table 3.1) and confectionary formulation guidelines (Heim 2003) were used to design three caramel model systems. Because the properties of the caramel coating system were of chief interest, popcorn and nuts were not included in the model system formulations. Salt and baking soda content were kept constant across all model systems and the batch size was set at 500 g. The caramels were prepared by heating and stirring all ingredients except for baking soda in a 2 L stainless steel saucepan over medium heat until the mixture reached a temperature of 150 °C, at which point the pan was removed from the heat source and baking soda was whisked into the mixture for 15 s. The

caramel mixture was then poured out onto an aluminum foil lined cookie sheet and allowed to cool at 22 °C.

Statistical analysis

Quantitative and qualitative data collected in the Napping-UFP exercise were used to perform factor mapping and hierarchical clustering of the caramel corn samples. The Napping data were formatted as outlined in Pagès (2005) and analyzed using Multiple Factor Analysis (MFA) in the FactoMineR (R version 3.0.1) statistical software package (Le and others 2008). Degree of similarity among caramel corn samples was visualized using factor maps, which show an average placement of samples based on aggregate relative positioning, or X- and Y-coordinates, of samples on each panelist's paper sheet. Factor maps were produced for each round or modality of the Napping-UFP exercise, global, aroma-by-mouth, texture, and taste (Figures 3.2-3.5). Hierarchical clustering was performed to produce a hierarchical tree relating and grouping sample clusters (Husson and others 2010). The optimal number of clusters for this sample group was determined visually using a scree plot and kept consistent for each napping exercise. Finally, 95% confidence ellipses were generated with 500 iterations per sample using the conf.R function written by Dehlholm and others, which employs the bootstrapping technique (Delholm and others 2012).

Analytical data collected for the samples, including water activity, moisture content, and thermal characteristics, were compared with UFP data generated during the Napping exercises via Spearman's correlation analysis using XLSTAT statistical software (Addinsoft USA, New York, NY, U.S.A.).

3.4 Results and discussion

Napping-UFP results

Factor mapping and hierarchical clustering analysis of Napping-UFP results provided an easy way to visualize the grouping and overall relatedness of caramel corn samples in the study. Projection of the hierarchical clustering tree over the factor map gave an integrated view of the MFA factors and hierarchical clusters and allowed for the selection of the optimal number of sample clusters - three. The organization of samples into three clusters for each sensory modality is shown in Table 3.2. These three clusters are also color-coded on the factor maps for each modality (Figures 3.2-3.5). Samples present in each of the three clusters differed from modality to modality, but a few key samples remained in separate clusters for all four exercises. Confidence ellipses overlap between some products of each cluster, but significantly, the confidence intervals of the key samples do not overlap when products were evaluated globally and by aroma-by-mouth and texture. These key samples (Product 9, Product 3 and Product 1, Product 4) were identified as representative samples, and anchor three distinct groups across which the spread of commercial caramel corn products can be distributed.

The three categories of commercial caramel corn products identified through this exercise can be described both by production scale and by dominant sensory characteristics identified by panelists during the UFP exercise. The term “small-scale” refers to products that are made with traditional ingredients for more local distribution and have relatively short shelf life, while the term “large-scale” refers to products that are mass-produced for widespread distribution and typically have longer shelf-life. The representative sample Product 9 anchors a group of small-scale caramel corn samples characterized by a rich, burnt, and buttery flavor

profile, hereafter referred to as the Small-Scale Dark group. The pair of similar samples Product 1 and Product 3 together anchor a group of large-scale caramel corn samples that are light in color, texture, and flavor with a dominant buttery note, hereafter referred to as the Large-Scale Light group. The final representative sample, Product 4, anchors a group of large-scale caramel corn samples that are dark in color and characterized by a molasses-like flavor, hereafter referred to as the Large-Scale Dark group.

Formulation of caramel model systems

Formulation of three commercially relevant caramel model systems that matched the key sensory properties of the targeted caramel categories identified in this study (Small-Scale Dark, Large-Scale Light, and Large-Scale Dark) was achieved. Exploration of the representative samples that exemplified the characteristics of each category revealed that the content and source of sugar (white sugar, brown sugar, and/or corn syrup) and lipid (butter, margarine, corn oil, soybean oil, and/or sunflower oil) accounted for the major differences among products of each category. Sugar and lipid sources for each representative sample are highlighted in Table 3.1.

All three commercial categories were found to contain corn syrup, and so all caramel model systems were formulated to include corn syrup as a sugar source. Additionally, the products in the Small-Scale Dark and Large-Scale Dark categories contain brown sugar, while the products in the Large-Scale Light group contain granulated sugar. The use of brown sugar contributes both color and the burnt or molasses-like flavor that characterize the Small- and Large-Scale Dark products and model systems. The type of lipid used in commercial caramel corn products was found to vary by category. Small-Scale Dark and Large-Scale Light products both contain

butter, which contributes significantly to the rich and buttery flavors identified by panelists in products from these categories. Vegetable oils, generally more economical lipid sources, are also found in the Large-Scale products. In response, Large-Scale Light and Large-Scale Dark caramel model systems are formulated to include soybean oil and corn oil, respectively. The final formulas for the three caramel model systems are given in Table 3.3.

Thermal and physical properties of commercial caramel corn samples

Results from analytical tests conducted to characterize the thermal and physical properties of the commercial caramel corn samples, including moisture content determination, a_w measurement, and DSC analysis (T_g and T_m parameters), are summarized for each commercial sample in Table 3.4. Generally, all of the products tested were low moisture and low a_w foods, with moisture contents ranging between 1.2 and 3.8% wet basis and a_w values ranging between 0.21 and 0.28.

Thermal analysis of the caramel coating systems, reported in Table 3.4, shows that all caramel coatings studied exhibit glass transition onset temperatures at or above 20 °C. This finding indicates that the caramel coating systems are primarily in the glassy amorphous state at room temperature. The representative samples, Product 9, Product 1, Product 3, and Product 4, have particularly high glass transition temperatures, with T_g onset values between 40 and 50 °C. High T_g values are desirable in caramel coating systems, as higher T_g values can be expected to correspond to a crisper coating texture, which is preferred in caramel corn products (Beck and others 2002).

Eight of the 12 caramel coating samples studied, including representative samples for the Small-Scale dark and Large-Scale dark categories, also exhibit an endothermic melting peak

(T_m, Table 3.4) indicative of the presence of crystalline sugar. Large-Scale light caramel corn samples may lack crystalline sugar because they contain a lower percentage of sugar and a higher percentage of corn syrup, which inhibits recrystallization of sucrose, in their coatings relative to Small- and Large-Scale dark samples (Tjuradi and Hartel 1995; Miller and Hartel 2015). DSC thermograms for caramel coating samples containing butter also exhibited an exothermic peak associated with the crystallization of butter ($T_{c\text{-butter}}$) during cooling.

Correlation data

Sixteen analytically determined variables, 8 of which are included in Table 3.4, and 26 sensory terms articulated by panelists during the Napping-UFP exercise were compiled for all twelve commercial caramel corn products to generate Spearman correlation coefficients for each pair of terms and variables. A total of 74 significant correlations were identified in this study.

Sensory descriptors that correlated significantly with analytical measures, highlighted in Table 3.5, are of particular interest due to our aim of validating UFP-generated sensory descriptors. Notably, three analytical measures (the enthalpy of melting of the caramel coating (ΔH_m), moisture content, and a_w) correlated positively with stickiness, indicating that, even using a flash descriptive profiling method, panelists were able to consistently identify samples with higher moisture contents and stickier coatings. The moisture content of the samples was also negatively correlated with the term “crispy”, which shows again that panelists were able to generate relevant textural terms that related directly to the composition of the samples.

A parameter associated with the exothermic crystallization of butter on cooling ($T_{c\text{-butter}}$ midpoint) was positively correlated with the sensory terms “mild” and “light”, which is likely

due to the lighter color and milder flavor of the samples made with butter and belonging to the Large-Scale Light group. As expected, the sensory term "crispy" correlates positively with T_g onset, midpoint, and endpoint values, though these correlations were not statistically significant at a significance level of α=0.05. Although further descriptive sensory analysis is required to fully understand the sensory properties of caramel corn products (Steiner and others 2003) and their relationship with key thermal, physical, and compositional properties of the samples, this study shows that a flash profiling technique, such as Napping-UFP, can be used to generate useful sensory terms which correlate to related analytical measures.

3.5 Conclusions

This study represents a novel application of the Napping-UFP method as a preliminary step in the formulation of model systems. The model systems derived in this study allow for easy experimentation and manipulation of commercially relevant caramel coating systems. Instrumentally measured properties of the caramel model systems will be presented in a future study. Utilization of the model systems developed can provide further insights into the effect of caramel composition on sensory and physical characteristics of the system and strengthen the bridge between sensory and physical properties of caramel coating systems.

The findings from this research has revealed some correlations between sensory descriptors and physical and thermal properties and composition of caramel coating systems, yet the meaning of the sensory terms is open to interpretation due to the informal method of term generation. The coating systems created through this study provide an opportunity for deeper exploration into the link between composition (i.e. sugar and lipid source and quantity)

and dominant sensory properties of the coating system. Descriptive analysis utilizing a trained panel could provide well-defined terminology and a more complete understanding of the sensory profile of caramel coating systems. Additional analytical techniques, such as texture analysis, could also be implemented to probe for relationships between the sensory profile and physical characteristics of these systems.

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3.7 Figures and tables

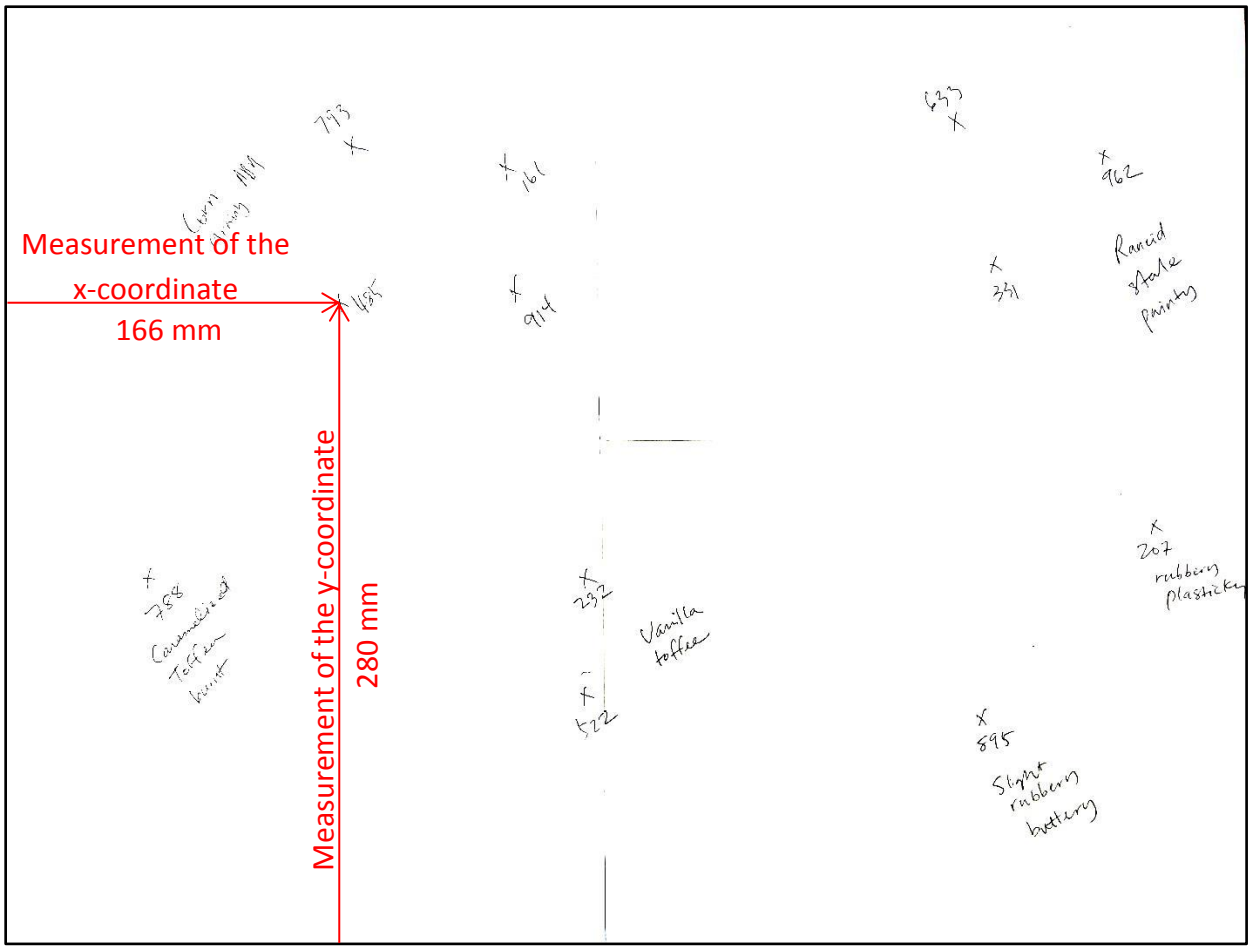

Figure 3.1. Example of Napping paper sheet used by panelists. Sample locations are marked with X's and labeled with corresponding 3-digit sample codes and descriptive terms. Coordinates for each sample are calculated by measuring the distance from the left edge to the center of the X (x-coordinate) and from the bottom edge to the center of the X (y-coordinate). An example calculation of x- and y-coordinates for sample 485 is shown in red.

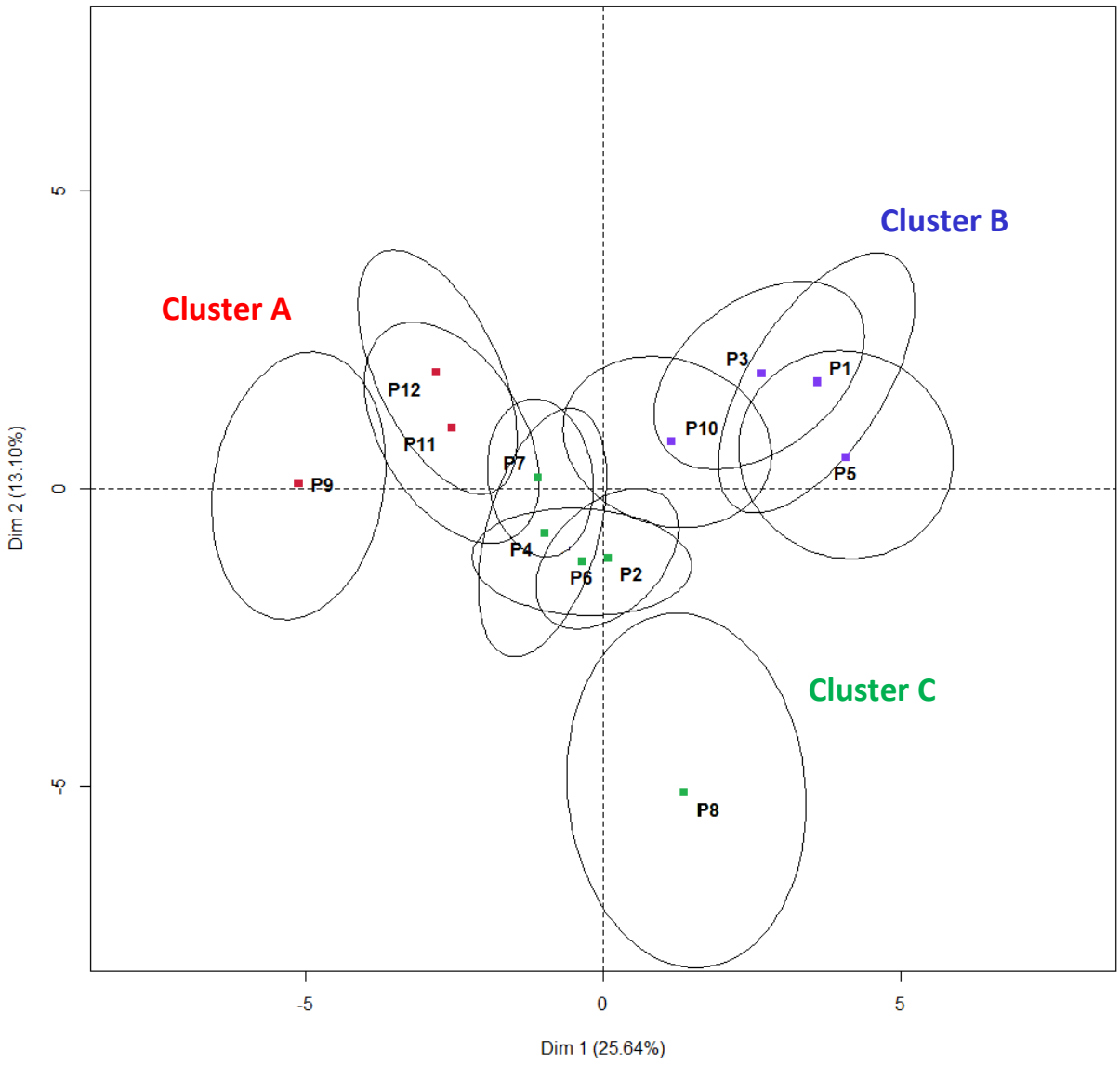

Figure 3.2. Factor map with 95% confidence ellipses for the 12 products from global Napping exercise plotted by degree of similarity. Products are color-coded according to cluster (Cluster A in red, Cluster B in purple, Cluster C in green).

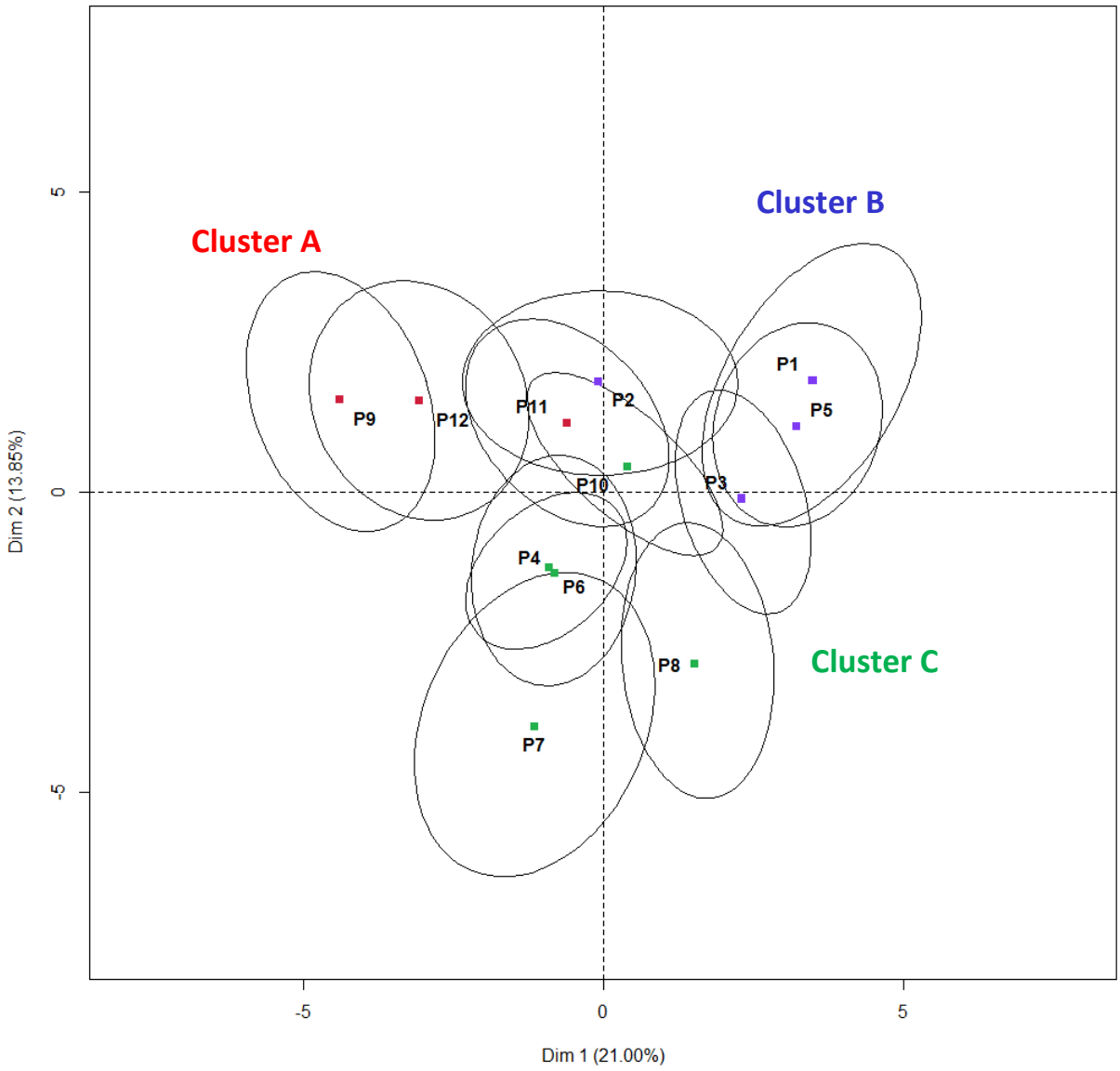

Figure 3.3. Factor map with 95% confidence ellipses for the 12 products from aroma-by-mouth Napping exercise plotted by degree of similarity. Products are color-coded according to cluster (Cluster A in red, Cluster B in purple, Cluster C in green).

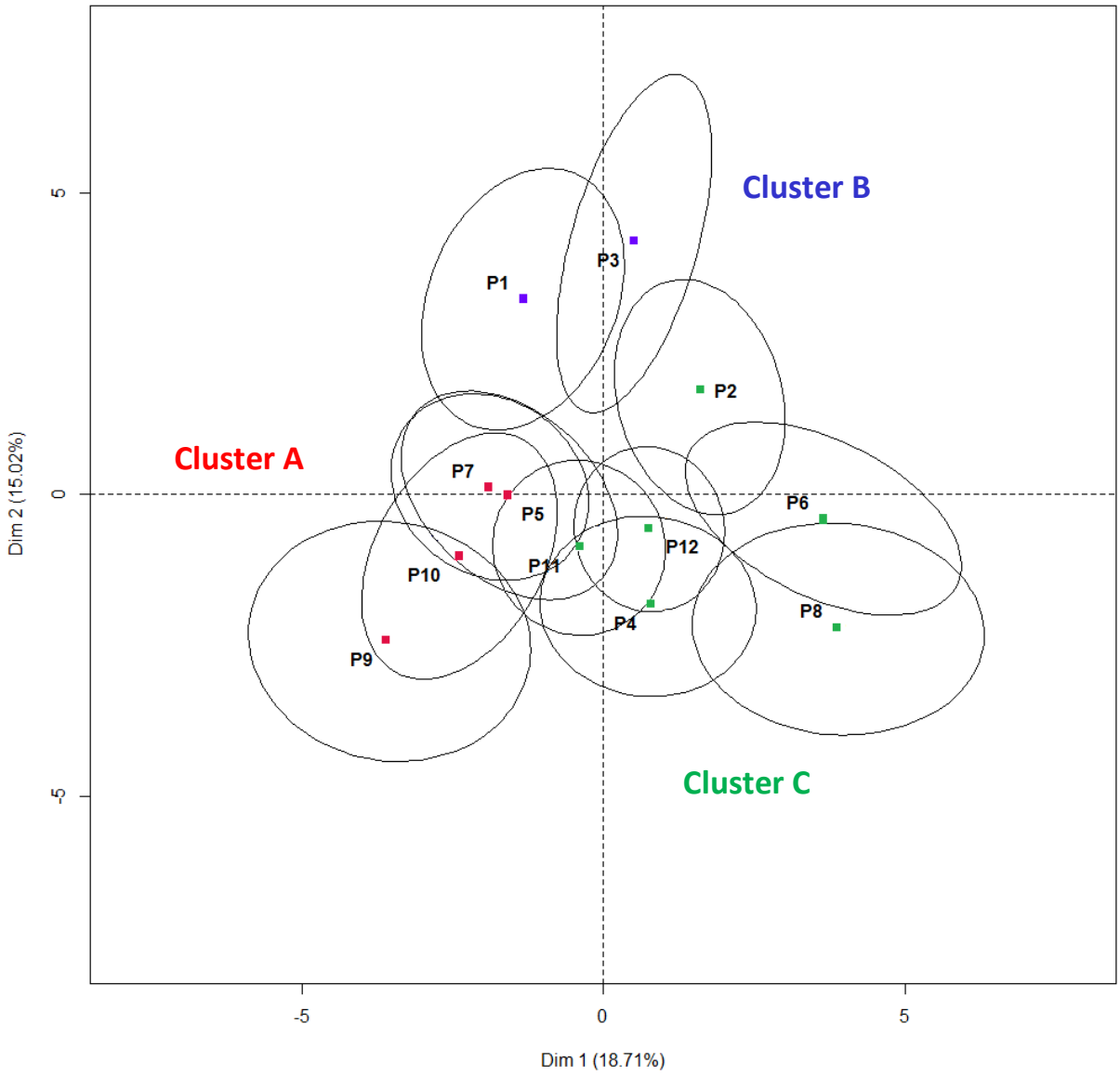

Figure 3.4. Factor map with 95% confidence ellipses for the 12 products from texture Napping exercise plotted by degree of similarity. Products are color-coded according to cluster (Cluster A in red, Cluster B in purple, Cluster C in green).

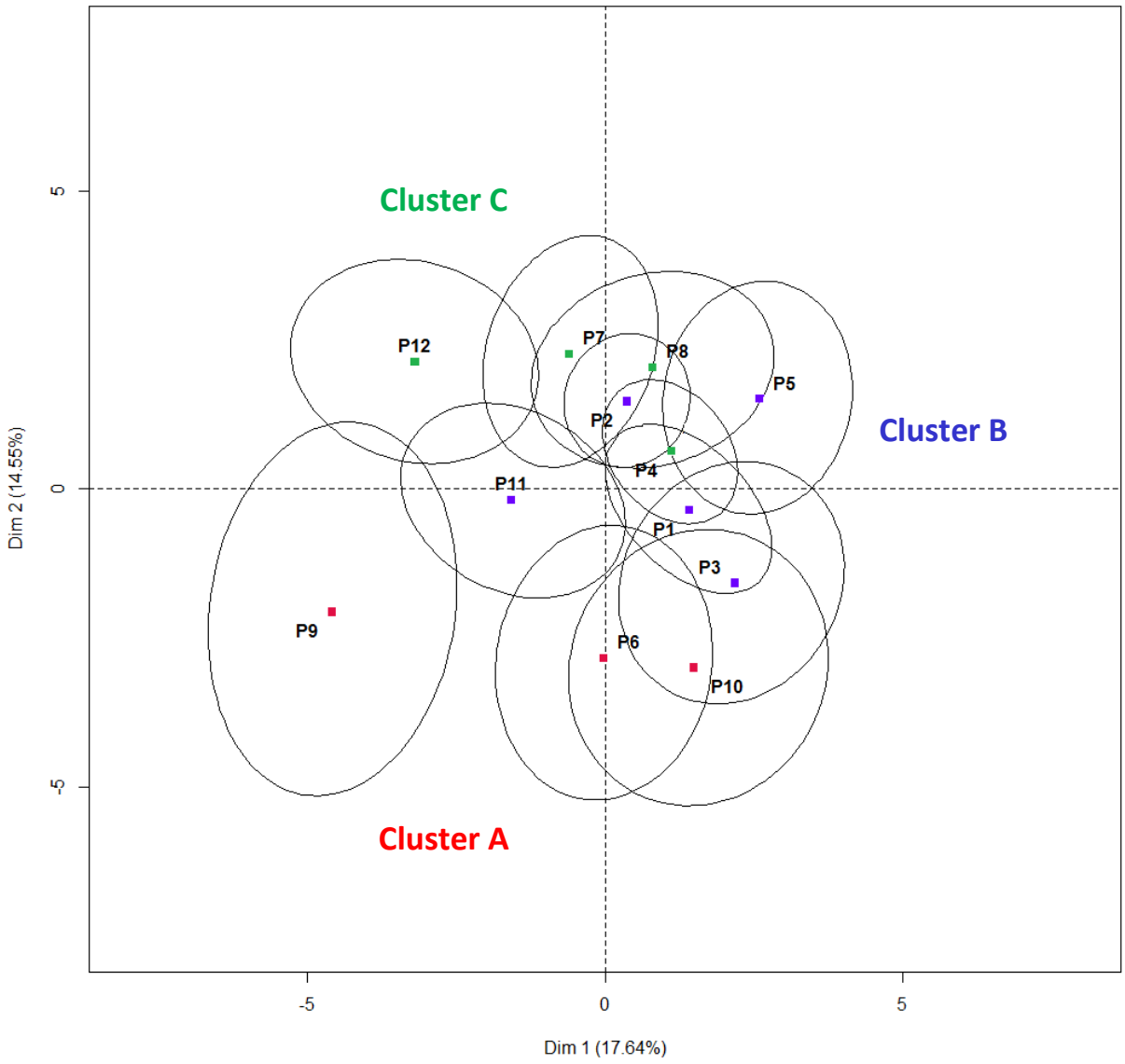

Figure 3.5. Factor map with 95% confidence ellipses for the 12 products from taste Napping exercise plotted by degree of similarity. Products are color-coded according to cluster (Cluster A in red, Cluster B in purple, Cluster C in green).

Table 3.1. Ingredient lists and pictures of representative samples which anchor product categories small-scale dark (product number 9), large-scale light (product numbers 1 and 3), and large-scale dark (product number 4). Ingredients are categorized into sugar sources, lipid sources, and other, and are listed in order of decreasing weight within their categories.

	Small-Scale Dark	Large-Scale Light		Large-Scale Dark
	Product 9	**Product 1**	**Product 3**	**Product 4**
				
Sugar Source	brown sugar corn syrup	corn syrup sugar	corn syrup sugar brown sugar	brown sugar corn syrup
Lipid Source	unsalted butte	butter margarine soybean oil	butter soybean oil	sunflower oil and/or corn oil
Other	popcorn water salt baking soda	popcorn peanuts soy lecithin salt sodium bicarbonate	almonds pecans popcorn salt soy lecithin	popcorn baking soda salt soy lecithin

Table 3.2. Products, denoted by product number, divided into three groups according to FactoMineR clustering analysis for each Napping exercise: global, aroma-by-mouth, texture, and taste. Global Napping clusters are designated Cluster A, B, and C and preserved according to the presence of the representative sample in bold and larger font.

	Cluster A	Cluster B	Cluster C
Global	**9**,11,12	**1**,**3**,5,10	2,**4**,6,7,8
Aroma-by-Mouth	**9**, 11, 12	**1**,**3**,5 2	**4**,6,7,8 10
Texture	**9** 5,10 7	**1**,**3**	2,**4**,6,8 11,12
Taste	**9** 10 6	**1**,**3**,5 11 2,	**4**, 8, 7 12
Representative Sample	**9**	**1**,**3**	**4**

Table 3.3. Ingredient lists and quantities for three caramel formulations, small-scale dark, large-scale light, large-scale dark, adapted from representative samples, product numbers 9, 1 and 3, and 4.

Small-Scale Dark (9)		**Large-Scale Light (1,3)**		**Large-Scale Dark (4)**	
Ingredient	**Quantity (g)**	**Ingredient**	**Quantity (g)**	**Ingredient**	**Quantity (g)**
brown sugar	240	corn syrup	150	brown sugar	245
butter	140	sugar	145	corn syrup	200
corn syrup	90	butter	125	corn oil	50
water	25	soybean oil	75	salt	2.5
salt	2.5	salt	2.5	baking soda	2.5
baking soda	2.5	baking soda	2.5		
Total mass:	500		500		500

Table 3.4. Thermal and physical properties of commercial caramel corn products included in Napping study, including onset, midpoint, and endpoint temperature of the glass transition (T_g), onset and midpoint of melting (T_m), enthalpy of melting, % wet-basis (wb) moisture content, and water activity (a_w). Moisture content and a_w values shown are averages from duplicate measurements.

Caramel Corn Products	**T_g onset, °C**	**T_g midpoint, °C**	**T_g endpoint, °C**	**T_m onset, °C**	**T_m midpoint, °C**	**ΔH_m (J/g)**	**Moisture Content (% wb)**	**a_w**
1	45.23	47.63	49.45	No melting transition observed			1.82%	0.255
2	47.33	49.51	51.68	No melting transition observed			1.30%	0.213
3	46.91	48.55	50.14	No melting transition observed			1.26%	0.229
4	41.86	43.99	46.20	148.80	156.17	14.87	1.95%	0.248
5	33.32	40.00	46.73	144.81	146.16	8.14	3.77%	0.278
6	37.60	40.03	42.62	152.54	160.56	7.24	2.48%	0.239
7	25.57	30.78	35.83	144.28	157.11	21.80	2.95%	0.259
8	20.07	26.24	32.56	No melting transition observed			1.61%	0.220
9	47.72	50.47	53.09	153.17	158.89	18.22	1.68%	0.245
10	21.08	26.16	31.40	144.74	145.09	7.27	3.44%	0.277
11	20.99	28.45	35.45	133.00	139.42	8.24	2.86%	0.255
12	35.35	40.66	46.19	148.01	155.31	5.98	1.53%	0.220

Table 3.5. Key analytical parameters of commercial caramel corn samples found to correlate significantly with sensory descriptors generated by panelists during Napping exercise. Sensory data was converted to a frequency value corresponding to the number of times a term was used to describe a given sample. All correlation coefficients listed are significantly different from 0 with a significance level of α=0.05.

Analytical Parameter	Sensory Term	Spearman Correlation Coefficient
Moisture content (% wb)	crispy	-0.706
	sticky	0.694
	mild	-0.591
a_w	sticky	0.731
T_g midpoint (°C)	matte	-0.585
T_g endpoint (°C)	matte	-0.641
T_m midpoint (°C)	firm	0.678
	gummy	0.766
ΔH_m (J/g)	crispy	-0.661
	sticky	0.683
$T_{c\text{-}butter}$ midpoint (°C)	light	0.710
	matte	-0.607
	mild	0.663

Chapter 4: Sensory and physical effects of sugar reduction in a caramel coating system

4.1 Abstract

Sugar reduction in processed foods is a pressing and complex problem, as sugars contribute important sensory and physical properties to foods. Composed of sugars and lipids, caramel coating systems, like the coating in caramel popcorns, exemplify this challenge. In order to probe the feasibility and consequences of sugar reduction, both sensory and physical properties were measured for three types of caramel coating systems. Four commonly used sugar alcohols, isomalt, maltitol, mannitol, and sorbitol, with different thermal properties and relative sweetness values were chosen to replace sugar in the caramel coating systems at 25% and 50% sugar reduction levels. Full sugar (control) and reduced sugar caramel coating samples were prepared in duplicate. Ten trained panelists participated in a six-week descriptive analysis panel to define and quantify the intensity of important sensory characteristics. All 24 sensory terms generated by the panel differed significantly across caramel type and sugar replacer. Thermal properties were measured through differential scanning calorimetry, and textural properties were measured through texture profile analysis. Replacement of sugar with sugar alcohols was found to decrease the glass transition temperature and systematically alter the hardness and resilience of caramel samples. Principal component analysis of sensory and physical data revealed that caramel coating type dictates caramel aroma, aroma-by-mouth, taste, and aftertaste, while sugar replacer and replacement level dictate texture. This research represents the first comprehensive study of the effects of sugar reduction in a caramel coating

system and suggests successful strategies for sugar reduction and key parameters to control in reduced sugar systems.

4.2 Introduction

Sweetness plays a large role in the overall palatability of a food product, which, in turn, profoundly influences intake and satiety (Sørensen and others 2003). Sugar replacers, also known as alternative sweeteners, are appealing because they provide sweetness sought by consumers without the calories or other adverse metabolic or cariogenic effects of sucrose (Flanyak 1991; Chattopadhyay and others 2014). A large demand for reduced sugar and sugar-free products has grown out of an intensified focus on health and desire for lower calorie foods, sparked by the current global obesity problem (Chattopadhyay and others 2014). Low sugar or sugar-free options are also important aids in regulating blood glucose levels for a growing diabetic population (Chattopadhyay and others 2014). While no single sugar replacer can match all functional roles of sucrose, sugar alcohols are a promising and frequently utilized choice for sucrose replacement in more demanding applications because they can approach some of the structural and bulking properties of sucrose, in addition to providing sweetness (Alonso and Setser 1994; Chattopadhyay and others 2014).

Caramels are a popular and ubiquitous confection or component of confectionary products, yet are significantly less studied in the literature compared to chocolate systems (Weir and others 2016). Caramel is an umbrella term that can be applied to a range of confectionary products, sauces, flavors, and colors that are tied to the caramelization reaction of sugars and/or the Maillard browning reaction of reducing sugars and amino acids. In this

research, the term “caramel coating” is used to refer to a carbohydrate- and lipid-based system, heated to the hard crack stage, and developed to resemble the coating material in caramel popcorn products (Beck and others 2002). As these caramel coating systems are composed almost entirely of sugar, corn syrup, and some lipids, they present a challenging case study in sugar reduction. Because sugar dominates the composition of the amorphous continuous phase of caramel coating systems, replacing sugar could profoundly impact physical properties of the sample, including sample geometry, degree of crystallinity, mouthfeel, and adhesiveness (Mendenhall and Hartel 2014; Miller and Hartel 2015). Reduced sugar or sugar-free caramel prototypes must then be carefully vetted through testing of samples against a control with well understood and accepted properties.

Validation of test samples through sensory testing yields the most reliable results as human evaluation can best predict consumer perception or acceptance. Utilizing trained panelists to describe and quantitatively evaluate key product attributes, descriptive tests provide the most complete sensory profile of samples (Stone and others 1974; Meilgaard and others 1991). Previous descriptive analysis of caramels has identified important textural attributes for differentiating between the texture of full-sugar samples made with varying amounts of sweetened condensed milk and palm kernel oil, including hardness, stickiness, and toothpacking (Steiner and others 2003).

Though no instrumental measurement can replace sensory testing, analysis of relevant physical properties is a good preliminary step in reduced sugar or sugar-free product formulation. Texture Profile Analysis (TPA) methods are often successful in predicting textural

properties, such as hardness, that are relatively simple to define in physical terms, but generally achieve more mixed results in predictions of complex textural properties, such as creaminess or stickiness (Breene 1975; Bourne 1978; Szczesniak 2002). Texture analysis methods have been applied to caramel products, but only one study was found that compared parameters to trained panel sensory data, and only one parameter (tack force) was reported to correlate significantly to a sensory property (stickiness) (Beck and others 2002; Steiner and others 2003; Gupta and others 2007; Krystyjan and others 2012). Rheological measurements of caramels have been reported to correspond well to sensory and physical properties of caramels, but these methods are not generally applicable to caramel materials near or in the glassy state (Chung and others 1999; Steiner and others 2003; Wagoner and others 2016).

Other commonly utilized instrumental predictors of sensory properties include thermal and moisture-related analyses. Glass transition temperature (T_g), measured via differential scanning calorimetry, has been explored and found to correlate significantly to several sensory properties, including hardness, crispness, and adhesiveness (Slade and others 1991; Martinez and Chiralt 1995; Huang and Hsieh 2005; Payne and Labuza 2005). Sample water activity and moisture content are also frequently measured and related to sensory properties of food materials (Roudaut and others 1998; Rousset and others 1999; Pereira and others 2002; Huang and Hsieh 2005; Payne and Labuza 2005; Kim and others 2009).

The first aim of this study was to characterize sensory and physical changes in caramel coating systems caused by sugar replacement with various sugar alcohols. Insight gained into the key effects of sugar replacement provided guidance for our second aim, which was to

correlate sensory and analytical texture measures of model caramel systems in order to identify useful physical predictors of sensory properties. We hypothesized that moisture content and water activity would correlate positively to sensory stickiness, glass transition temperature would correlate negatively to sensory stickiness, and TPA parameters of hardness, adhesiveness, cohesiveness, and fracturability would correlate positively to sensory texture properties of force to pierce, stickiness, cohesiveness, and crumbliness, respectively, in the model caramel coating systems.

4.3 Materials and methods

Caramel preparation

Caramel coatings used in commercial caramel popcorn products are generally composed of some combination of sugars (corn syrup, sugar, brown sugar) and lipids (butter, vegetable oils). The precise formula and sensory properties vary by product, but the coatings of the caramel popcorn products are generally crisp in texture and present a caramelized flavor. In previous work, the Napping-Ultra Flash Profile method was used to identify and characterize three leading categories of commercial caramel corn products (Mayhew and others 2016). These categories were assigned names based on the scale of production (small or large) and the depth of color and flavor (dark or light). The first category, Small-Scale Dark, was characterized by a rich and burnt flavor profile and encompassed the products that were made by boutique producers. The other categories, Large-Scale Light and Large-Scale Dark, captured the products sold through grocery store chains. The Large-Scale Light category described products with a light and buttery profile, while the Large-Scale Dark category included products with a sweet

and molasses-like profile. The caramel coating composition of anchor samples in each category was used to create formulas for three model systems which represent each category of caramel coating (Mayhew and others 2016). The formulas for full and reduced sugar samples are given in Table 4.1, and ingredient information is provided in Table 4.2. Control batches were made with a combination of sugar, brown sugar, and corn syrup. The corn syrup used to produce these samples had a relatively high dextrose equivalent (DE) value, between 60 and 67, a moisture content of approximately 20% (wet basis), and was sold under a food service brand. Reduced sugar batches, in which 25 or 50% of sugar was replaced in each coating system category with one of four sugar alcohols (isomalt, maltitol, mannitol, sorbitol), were also formulated and produced. The total sugar was calculated as the sum of sugar or brown sugar and the sugar present in the corn syrup (50% monosaccharides and disaccharides by weight), but only the sugar or brown sugar was replaced by sugar alcohols in order to maintain consistent moisture and corn syrup solid content.

The caramel samples were prepared by heating and stirring all ingredients, except for baking soda, in a stainless steel saucepan over medium heat and monitored using a high accuracy Traceable® thermocouple (Thermo Fisher Scientific Company, Waltham, Massachusetts, U.S.A.) until the mixture reached a temperature of 150°C, at which point the pan was removed from the heat source and baking soda was whisked into the mixture for 15 seconds. The caramel mixture was then poured out and spread into silicone miniature cube trays (WOOTOP, Shenzhen, Guangdong, China) to produce standardized 1.0 cm^3 cubes, covered with aluminum foil, and allowed to cool at room temperature. Each sugar replacer and replacement level combination (1 full sugar control, 8 reduced sugar) in each coating system

category (Small-Scale Dark, Large-Scale Light, Large-Scale Dark) was produced in duplicate to control for possible batch effects (54 total batches). Cooled samples were removed from trays and vacuum sealed (FoodSaver, Sunbeam Products, Inc., Boca Raton, Florida, U.S.A.). Vacuum sealed packs were stored in an opaque tub with a tight-fitting lid to minimize undesirable changes in the sample over time, such as changes in moisture content or oxidation.

Samples are coded by formula type (SD for Small-scale Dark, LD for Large-scale Dark, LL for Large-scale Light) – sugar replacer (C for full-sugar Control, I for Isomalt, M for Maltitol, N for maNnitol, S for Sorbitol) – sugar replacement percentage (0, 25, 50).

Descriptive analysis

Ten panelists (4 male, 6 female; ages 22 to 55 yrs.) were screened for basic taste sensitivity and recruited to join a six week descriptive analysis (DA) panel. Over the course of the study, panelists were trained to evaluate 27 distinct caramel samples with varying sensory profiles. In the first four weeks of the study, panelists met for one hour each day and were introduced to DA methodology and participated in term generation and refinement, reference selection and scaling, group sample evaluation practice, and panel calibration exercises. A rotating, balanced subset of caramel samples was provided each day for panel training and practice.

In the final two weeks of the study, panelists evaluated samples individually in climate controlled booths lit with incandescent light and held at 22°C and 33% relative humidity. Panelists were instructed to recalibrate themselves with freshly prepared reference samples before each evaluation session, and references were labeled with their identity and served in

plastic cups with lids (Solo Cup Company, Inc., Chicago, IL, U.S.A.). Five sample cubes (1 x 1 x 1 cm^3) were served for each evaluation in plastic 29.5 mL cups with lids (Solo Cup Company, Inc.) and labeled with randomized three-digit codes. Attributes generated and evaluated by the panel are listed along with references, definitions, and evaluation instructions in Table 4.3. All attributes and references were rated on a scale of 0 to 15, and all 54 samples (2 batch replicates each of 27 samples) were evaluated in duplicate. Sample presentation order during booth testing was randomized across panelists using a William's Latin Square design (Williams 1949). Between each evaluation, panelists cleansed their palates with a prescribed rinse protocol of warm water (40 $\pm$ 5°C), baby carrot, warm water (40 $\pm$ 5°C), carbonated water, and room temperature water (23 $\pm$ 3°C). All rinses and samples were expectorated to ameliorate panelist fatigue. Panelists evaluated 6 samples per session and participated in two 30-minute sessions each day with at least 30 minutes rest between sessions. Data collection was conducted using the software system Compusense® Five (Version 5.0: Guelph ON, Canada).

Instrumental measurement of physical properties

Water activity (a_w) was measured in triplicate for each batch of caramels at 25.0 $\pm$ 0.1°C using an AquaLab 4TE instrument (Decagon Devices, Inc., Pullman, Wash., U.S.A.). Samples were prepared to maximize surface area and facilitate equilibration. Hard caramel samples were crushed and spread in cups, while soft caramels samples were formed to bottom of sample cups. Sample a_w was measured within 10 minutes of sample preparation to minimize water sorption or loss. Additionally, measurements were taken in the relatively dry months of February and March, and the relative humidity of the room was monitored. Trends in environmental humidity were not found to correspond to trends in a_w measurements.

Moisture content was measured for each caramel batch in triplicate via mass loss calculations following complete drying in a vacuum oven. Before analysis, hard caramel samples were ground to a fine particulate with a mortar and pestle and massed in a dry aluminum pan, while soft caramel samples were massed and spread across the base of a dry aluminum pan. Sample pans were then loaded on trays and placed in a vacuum oven. The pans were arranged randomly on trays in order to minimize the effect of any temperature gradient within the oven. Samples were held under full vacuum at 60°C for 24 hours. Weight loss between the original and dried samples was measured and average percent moisture content (wet basis, wb) calculated for each sample.

Differential scanning calorimetry (DSC) was employed to characterize the thermal profile of caramel samples. A calibrated DSC Q2000 instrument with an autosampler (TA Instruments, New Castle, DE, U.S.A.) and a refrigerated cooling system (RCS 90) was used for all data collection. An indium reference was used for instrument calibration (known melting temperature: $T_{m\ onset}$ of 156.6°C; known enthalpy: ΔH of 28.71 J/g). All test and calibration runs were performed under a dry nitrogen purge gas at a flow rate of 50 mL/min.

Two replicates from each caramel batch (or a total of four replicated from each formulation) were prepared either by crushing with a mortar and pestle (hard samples) or cutting with a metal spatula (soft samples) to achieve a consistent sample size, then hermetically sealed in aluminum Tzero pans with lids (TA Instruments). Caramel samples (8 ± 2 mg) were equilibrated at -40°C, then heated at a rate of 10°C/minute to 200°C. All DSC scans were analyzed using Universal Analysis software (Version 4.4A, TA Instruments) to determine

parameters associated with the glass transition (T_g), physical aging (ΔH, J/g), melting of butter ($T_{m\text{-butter}}$), and the melting (T_m) of the coating system upon heating. Peaks in the thermograms were analyzed using the Integrate Peak Sigmoidal Horizontal function and transitions were analyzed using the Glass/Step Change function. A peak corresponding to the melting of butter was observed and measured; however, this data is not reported because it did not aid in the differentiation of the samples.

All carbohydrate ingredients used in the formulas were also analyzed to provide a reference for system T_g measurements. Ingredient samples (9 ± 1 mg) were prepared similarly to caramel samples, in Tzero aluminum pans with hermetic lids (TA Instruments). Two general protocols were used depending on the initial state of the ingredient, as ingredients in the solid state had to be melted and quickly cooled to form amorphous material prior to determination of the T_g. Ingredients in the solid state were first heated to approximately 5°C above the reported melting temperature of each material at a rate of 10°C/minute in the DSC and rapidly cooled to -50°C to form amorphous material with minimal decomposition, then heated at a rate of 10°C/minute to 25°C above the reported melting temperature to allow for T_g determination and detection of any residual crystalline material. The final temperature for the first and second heating procedure of each solid ingredient were as follows: beet sugar (200°C, 220°C), brown sugar (200°C, 220°C), isomalt (160°C, 180°C), maltitol (155°C, 175°C), mannitol (180°C, 200°C), and sorbitol (105°C, 125°C). Samples of corn syrup (12 ± 1 mg), the only non-solid carbohydrate ingredient tested, were equilibrated at -80°C to form a glass, then heated at a rate of 10°C/minute to 40°C. Ingredient glass transitions were analyzed in Universal Analysis software (Version 4.4A, TA Instruments) with manual tangent selection in the Glass/Step

Change function. The average standard deviations for T_m onset, glass transition temperature, and change in specific heat (Δc_p) measurements were 0.80°C, 0.71°C, and 0.0099 J/g/°C, respectively.

Texture analysis was employed to measure physical properties related to the texture of caramel coating system samples. Measurements were made using the Texture Profile Analysis (TPA) two-bite compression test on a TA-XT2 Texture Analyser with a 50 kg load cell capacity (Texture Technologies Corp., Scarsdale, NY, U.S.A.). Sample cubes of approximately 1 x 1 x 1 cm^3 and 1.1 ± 0.2 g were centered on the TA-XT2 platform at the start of each test, and the platform was wiped clean with a Kimwipe (Kimberly-Clark Professional, Roswell, GA, U.S.A.) between each run to remove sample residue. A 2 inch cylindrical probe was used for compression with a test speed of 1.0 mm/s and a compression distance of 10%. Six replicates were taken for each of 54 total sample batches. Texture properties (Fracturability, Hardness, Adhesiveness, Springiness, Resilience, Gumminess, and Chewiness) were calculated as advised by Texture Technologies, adapted from Bourne's Food Texture & Viscosity (Bourne 2002).

Statistical analysis

Sensory and instrumental data were analyzed for sample and sample group differences using the Generalized Linear Model procedure in SAS (Version 9.2, SAS, Cary, NC, U.S.A.) to conduct Analysis of Variance (ANOVA) and means separation. Radar plots were generated using Microsoft Excel (Microsoft Corporation, Seattle, WA, U.S.A.). Principal Component Analysis (PCA) of sensory data, using Pearson's correlation and Varimax rotation, and Pearson's

correlation of sensory and physical data were conducted using XLSTAT (Addinsoft, New York, NY, U.S.A.). A significance level of 0.05 was used for all judgments.

4.4 Results and discussion

Descriptive analysis

Significant differences were found for each of the 24 measured sensory attributes across individual samples, formula types, and sweeteners. Significant differences were also found among the judges and for the judge*sample/formula type/sweetener interaction factors, but statistical significance in differences across samples/formula types/sweeteners was preserved in every case after adjusting for these significant interactions. Attribute mean ratings and least significant difference (LSD) values are summarized by formula type and by sugar replacer and replacement level combination (Tables 4.4 and 4.5). Standard deviation values are available in Appendix A.

Control formulas, those with no sugar replacement, for the three formula types differed significantly in 18 of the 24 measured attributes. These differences in the sensory profile of each formula type are shown in Figure 4.1. The sensory profiles of the control formulas diverge most noticeably for aroma, appearance, aftertaste, and aroma by mouth attributes. Dominant attributes for the three formula types include burnt sugar aroma and aroma by mouth for SD, molasses-like aroma by mouth and sweet taste and aftertaste for LD, and browned butter and butterscotch aroma by mouth attributes for LL. Similar trends in sensory changes due to sugar replacer and replacement level were observed in each formula type, so only SD formula samples are presented as a representative case in Figure 4.2. SD samples differed significantly

for all 24 attributes assessed, though the largest differences in sample mean scores due to sugar replacement are found for texture attributes crumbly, sticky, and cohesive. In general, samples made with sorbitol (S) and mannitol (N) appear to differ most from the control sample.

To simplify the interpretation of sample, formula type, and sweetener differences, PCA was conducted for all sensory data and for subsets of data grouped by sensory modality. PCA factor loadings are available in Appendix B. The PCA biplot of the first two factors of aroma and aroma-by-mouth attributes explained 81.05% of the total variation and showed strong grouping of samples by formula type (Figure 4.3). Factor 1 was described by the presence (+) or absence (-) of flavor attributes related to butter, while Factor 2 was described by the presence of oxidized flavor attributes (+) or burnt sugar or molasses-like flavor attributes (-). SD samples were concentrated in the fourth quadrant and characterized by the presence of buttery and burnt sugar or molasses-like flavor attributes; LD samples were concentrated in the third quadrant and characterized by the absence of buttery flavor attributes and the presence of burnt sugar or molasses-like attributes; LL samples were concentrated between the first and second quadrant and characterized by a moderate presence of buttery flavor attributes, the presence of oxidized flavor attributes, and a relative absence of burnt sugar or molasses-like flavor attributes.

The same analysis was conducted with texture attributes, and 86.58% of the total variation was distributed between the first two factors (Figure 4.4). Factor 1 was described by a gradient from sticky, cohesive texture attributes (+) to crumbly texture (-), while Factor 2 appears to be a measure of hardness, with texture terms force to pierce sample and

toothpacking heavily loaded in the positive direction. When texture attributes were used as the differentiating variables, samples clustered by sweetener instead of by formula type. Full-sugar control samples and samples made with isomalt (25% or 50% replacement), maltitol (25% or 50% replacement), or mannitol (50% replacement only) fell between the second and third quadrant and were characterized by a crumbly texture and intermediate hardness. During term generation discussions, panelists also reported that N50 samples presented a mouth-cooling effect, although this attribute was not included in the final attribute list because it applied to only a narrow subset of the samples. Samples made with 25% replacement of sugar by mannitol or sorbitol fell in the first quadrant and were characterized by sticky, cohesive, and hard texture attributes. Finally, samples made with 50% replacement of sugar by sorbitol fell in the fourth quadrant and were characterized by sticky and cohesive texture attributes and low hardness.

Physical properties

Instrumental data relevant to texture and product stability were collected to gauge the impact of sugar replacement on physical properties of caramel coating systems. Physical differences due to sweetener were found within formula types for sample a_w, moisture content, thermal properties measured via DSC, and TPA parameters. Standard deviation values for each instrumentally measured parameter are omitted from data tables to increase table readability, but are available in Appendix C.

Water-related properties

All samples fell in a shelf-life stable range with respect to water activity; the highest sample a_w measured was 0.33, while the vast majority of samples fell between an a_w of 0.1 and 0.2. Statistically significant differences among the a_w of samples were observed; however, these differences did not follow any patterns or trends with regard to sweetener or formula type, and large batch variations were sometimes observed, indicating that the effect was likely random.

The moisture content of samples ranged from 0.58 to 2.23% wet basis, and samples made with mannitol and sorbitol showed consistently higher moisture contents (Table 4.6). There are a few possible explanations for the observed differences in moisture content. One is that samples in which sucrose, a 12-carbon molecule, is replaced by an equal mass of mannitol or sorbitol, both 6-carbon molecules, will result in greater depression of the boiling point and increase in the final moisture content due to the increase in the total moles of solute. However, this explanation would be supported in increase in moisture with increasing substitution of sucrose with mannitol or sorbitol. This trend is not observed. Another explanation for the increase in moisture for mannitol and sorbitol-containing samples is the softer nature of those samples, due to a lower glass transition temperature (T_g), which may have contributed to greater volatile loss during vacuum oven drying. This theory is supported by the data in that samples made with mannitol and sorbitol are the most rubbery and have the highest measured moisture content values; however, this theory does not explain the large gap in moisture content between samples made with maltitol and mannitol, which have a more moderate difference in the T_g. It also fails to explain the observed trend of higher moisture content values in samples made with mannitol relative to samples made with sorbitol. Differences in sample

hygroscopicity could be an additional factor; sorbitol is reported to be more hygroscopic than mannitol, and its presence in samples may result in less moisture release on drying (Alonso and Setser 1994). It is likely that all three of these explanations factor into the observed differences in moisture content to some extent. It should also be noted that the observed increases in moisture content of sample made with mannitol and sorbitol did not translate to corresponding increases in water activity.

Thermal properties

Glass transition (T_g) parameters and the onset of melting for each carbohydrate ingredient are summarized in Table 4.7. Experimental procedure, moisture content, and ingredient specifications can have a significant effect on the T_g of materials; consequently, reported T_g values for the ingredients studied vary widely in the literature. Glass transition temperature values determined for sucrose and sorbitol are similar to previously reported values (Yu and others 1998; Vanhal and Blond 1999; Lee and others 2011; Ghosh and Sudha 2012). However, T_g values determined experimentally for isomalt and maltitol were substantially lower (approximately 16°C and 10°C, respectively) than values reported in the literature; these deviations could be due to variations in the composition of the ingredients between suppliers (Cammenga and Zielasko 1996; Bustin and Descamps 1999; Borde and Cesàro 2001; Lappalainen and Pitkänen 2006). The T_g of sucrose is the highest of the ingredients included in this study, followed by brown sugar, isomalt, maltitol, sorbitol, and finally corn syrup. Due to the strong tendency of mannitol to crystallize, rather than form a glass, no T_g for mannitol could be determined experimentally in this study. By combining mannitol in varying concentrations with sorbitol, a glass-former, Yu and others (1998) have

calculated the T_g onset, midpoint, and endpoint of mannitol to be 10.7°C, 12.6°C, and 18.4°C, respectively, and the change in specific heat at the T_g to be 1.27 J/g/K. Based on the fact that all sugar alcohol ingredients utilized were measured to have a lower T_g than the sucrose and brown sugar used in this study, we can predict that incorporation of sugar alcohols into the caramel coating formulas should lower the overall system T_g relative to the control formula.

All samples were identified via DSC analysis to be in an amorphous solid state, with the exception of the N50 samples which contained both crystalline and amorphous material (Table 4.6). In samples made with butter (SD and LL formula types), two peaks corresponding to the endothermic melting (15 to 20 °C and 35 to 40 °C) of butter sometimes overlapped with the glass transition temperature range (Tomaszewska-Gras 2012). For this reason, a degree of uncertainty may be associated with glass transition temperature values extracted from SD and LL DSC thermograms. The low variability between measurements (average standard deviation of 1.1°C) and strong degree of similarity in trends between LD glass transition data and that of SD and LL formula samples supports the conclusions drawn about the effect of sugar replacement on the glass transition across all formula types. The general trend can be summarized as follows: the glass transition temperature of the samples decrease with sugar replacer T_g and with increased sugar replacement level (C0 < I25 ≈ I50 < M25 < M50 < N25 ≈ N50 < S25 < S50) (Table 4.6). Samples made with isomalt or maltitol remained in the glassy state at room temperature, but samples made with mannitol or sorbitol exhibited a large degree of plasticization and underwent the transition from the glassy to the rubbery state below room temperature.

Texture profile analysis properties

Characterization of samples via the TPA method was challenging due to the diversity of sample textures in this study; however, statistically significant and meaningful differences in TPA properties were found between samples of different formula types and sweeteners (Table 4.8). Specifically, the wide range of sample hardness constrained the selection of the compression distance (10%) in order to maintain consistent test parameters across all samples. Additionally, some TPA parameters only applied to a subset of the samples that display the textural property approximated by TPA; for example, the parameter "fracturable" only applied to brittle samples. Therefore, although average values for all TPA parameters measured are given for each sample, it should be noted that some of the parameters do not have practical relevance for all samples.

Formula type differences were observed primarily across small-scale and large-scale formulas; SD samples show higher average values for fracturability, resilience, chewiness, and cohesiveness. Sweetener differences were sporadic and often not maintained across formula types. TPA properties hardness and resilience showed the most consistent sweetener effects; M50 was the hardest, while S25/50 samples were the least hard, and N25/50 and S25/50 samples were least resilient across all formula types (Table 4.8). Sample T_g trends can be used to explain observed differences in sample hardness and resilience: samples that were glassy (T_g > room temperature), but not brittle have the highest TPA values for hardness; samples with the highest T_g were both glassy and brittle, and thus exhibited intermediate TPA hardness; rubbery samples (T_g < room temperature) were the least hard and the least resilient, due to the ease of sample deformation upon compression. SD-S25, LD-M50, and LL-S50 were highest in

their formula types for adhesiveness, with S25/50 samples generally high in adhesiveness, although sample and replicate variability were particularly high for adhesiveness (Table 4.8). Fracturability was not measurable in the majority of samples and showed little alignment with expected trends from sensory crumbliness.

The limitations of the TPA method in the characterization of this sample set were caused by the large range in physical properties of the sample set. Despite this limitation, some meaningful trends which could be intuited or explained by other known sample properties emerged. There is, therefore, reason to believe that correlations between TPA and sensory properties merit interpretation.

Correlational studies

Significant correlations were found between sensory texture terms and relating sensory terms to instrumentally measured physical properties (Table 4.9). Relationships between sensory terms are intuitive; sensory attributes sticky and cohesive have a strong positive correlation, and they are negatively correlated with crumbly. Toothpacking and force to pierce sample showed a weak, but statistically significant, positive correlation to each other, and neither term was strongly correlated to any other variable. TPA data showed relatively weak correlations to sensory texture data. As predicted, TPA hardness and adhesiveness showed significant positive correlations to sensory force to pierce and stickiness, respectively, but the magnitude of the correlations were low (≤ 0.4). Adhesiveness also showed significant but low magnitude correlations to sensory crumbliness (-0.391) and sensory cohesiveness (0.394). TPA measures of chewiness and resilience correlated significantly to sensory properties crumbly (+) and to sticky and cohesive (-); the direction of these correlations contradicts with general

understanding of the properties chewiness and resilience and suggests that while statistically significant, these correlations are not practically meaningful. No significant correlations were found between sensory measures of texture and TPA parameters cohesiveness and fracturability.

Water-related and thermal properties showed generally stronger correlations to sensory texture properties than TPA properties. Increased moisture content was correlated to increased sensory stickiness and cohesiveness and decreased crumbliness. This relationship makes intuitive sense; however, it should be noted, as discussed previously, that the higher values for moisture content measured for samples made with mannitol or sorbitol may be due in part to structural differences in those samples relative to the rest of the sample set. No significant correlations between a_w and sensory properties were identified.

Onset, midpoint, and endpoint T_g values showed strong and similar positive correlations with crumbly and negative correlations with sticky and cohesive. In other words, as sample T_g shifted the physical state of the sample from glassy to rubbery, sensory texture properties shifted from crumbly to sticky and cohesive.

4.5 Conclusions

Caramel coating samples that varied widely in sensory profile were produced by varying the sugar and lipid quantity and type. Principal Component Analysis biplot of factor 1 and 2 of sensory data showed that formula type is the biggest driver of sample differences overall and for aroma, aroma-by-mouth, taste, and aftertaste attributes, while the sweetener (sugar replacer and replacement level) drives differences in texture. Therefore, special attention

should be paid to maintenance of desired texture when formulating for sugar reduction in caramel or confectionary systems. Overall, isomalt most closely matched the sensory and physical contributions of sucrose in the caramel coating systems studied, and few measurable differences existed between samples with 25% and 50% sugar replacement with isomalt.

Instrumental measures surveyed (a_w, moisture content, T_g, and TPA) were generally unable to fully predict changes in texture caused by sugar replacement. The difficulty encountered in characterizing the diverse texture profiles of samples in this study via a uniform TPA protocol provided motivation to explore alternative physical characterization approaches. Considering all instrumental metrics investigated, T_g, which correlated strongly to crumbly, sticky, and cohesive textural properties, shows the most promise as a parameter for predicting the effect of sugar replacement on sensory textural properties.

In this study, five important sensory texture properties were measured; however, the measured properties present an oversimplified view of the complete, dynamic textural profile of the samples. In order to tailor instrumental measures to the sensory perception of texture, the temporal textural profile should be fully characterized. The low magnitude of the correlation between TPA adhesiveness and sensory stickiness also points to a question about the meaning and measurement of stickiness from a sensory perspective. What does stickiness perception encompass, beyond surface adhesion, and is panelist training with narrow definitions and references biasing panelists towards evaluation of specific facets of stickiness? These questions must be addressed to complete the picture of texture perception and suggest

best approaches for instrumental prediction of textural changes in full and reduced sugar caramel coating systems.

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4.7 Figures and tables

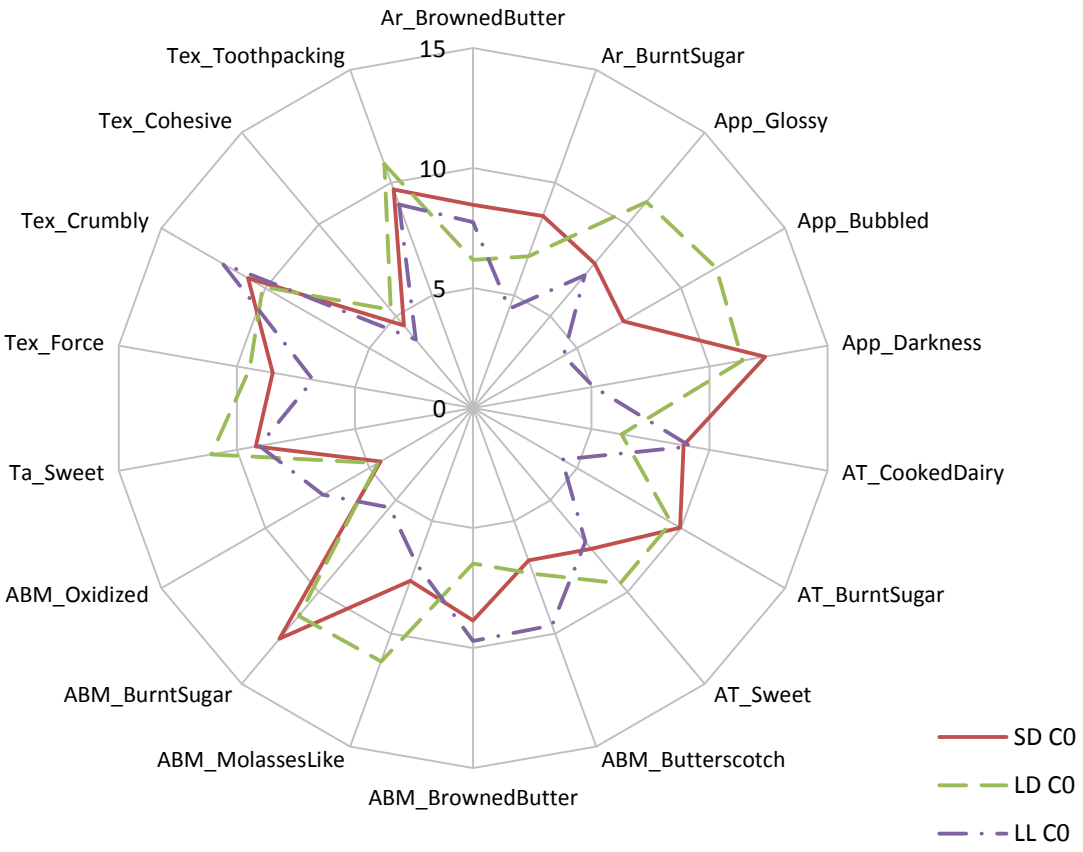

Figure 4.1. Spider plot showing average attribute intensity scores for SD, LD, and LL control formula samples for each attribute in which significant differences between control formulas were found (α=0.05). Attributes were evaluated on a scale of 0 to 15. Attribute modalities are indicated by prefixes: Ar for aroma, App for appearance, AT for aftertaste, ABM for aroma by mouth, Ta for taste, and Tex for texture. SD stands for small-scale dark; LD stands for large-scale dark; LL stands for large-scale light; C0 stands for control.

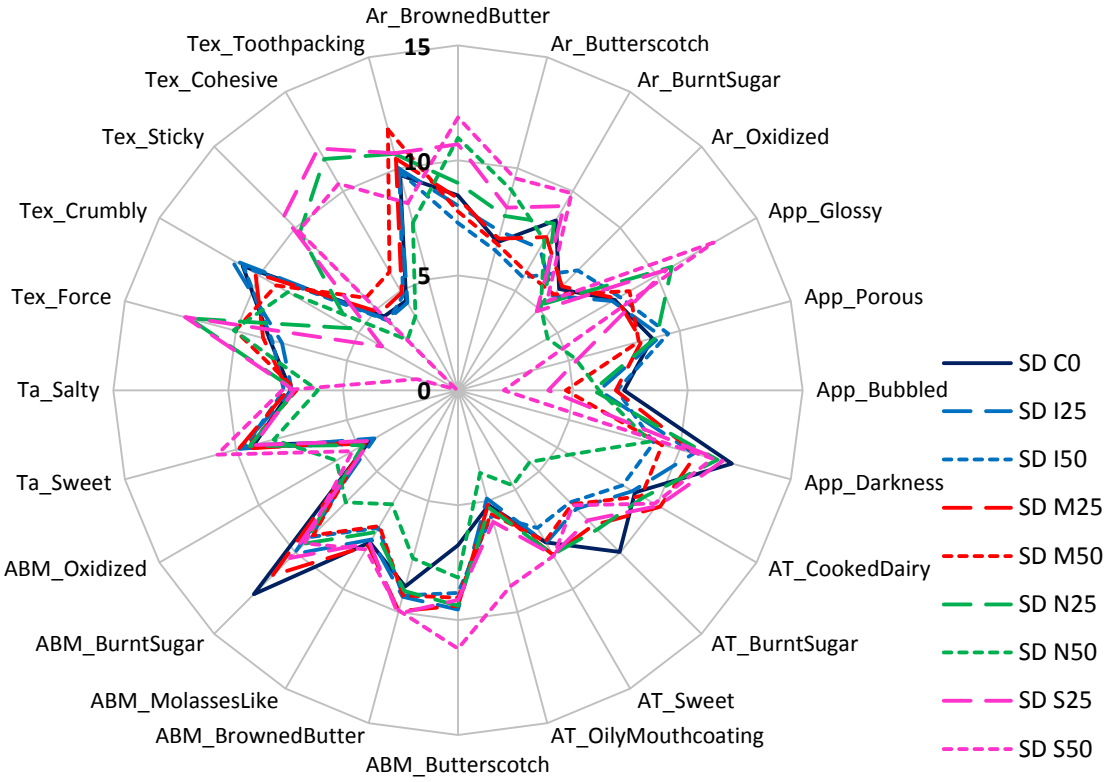

Figure 4.2. Spider plot showing average attribute intensity scores for all SD samples for each attribute in which significant differences between samples of the SD formula type were found (α=0.05). Attribute modalities are indicated by prefixes: Ar for aroma, App for appearance, AT for aftertaste, ABM for aroma by mouth, Ta for taste, and Tex for texture. SD stands for small-scale dark; C0 stands for full-sugar control; I stands for isomalt; M stands for maltitol; N stands for mannitol; S stands for sorbitol; 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol.

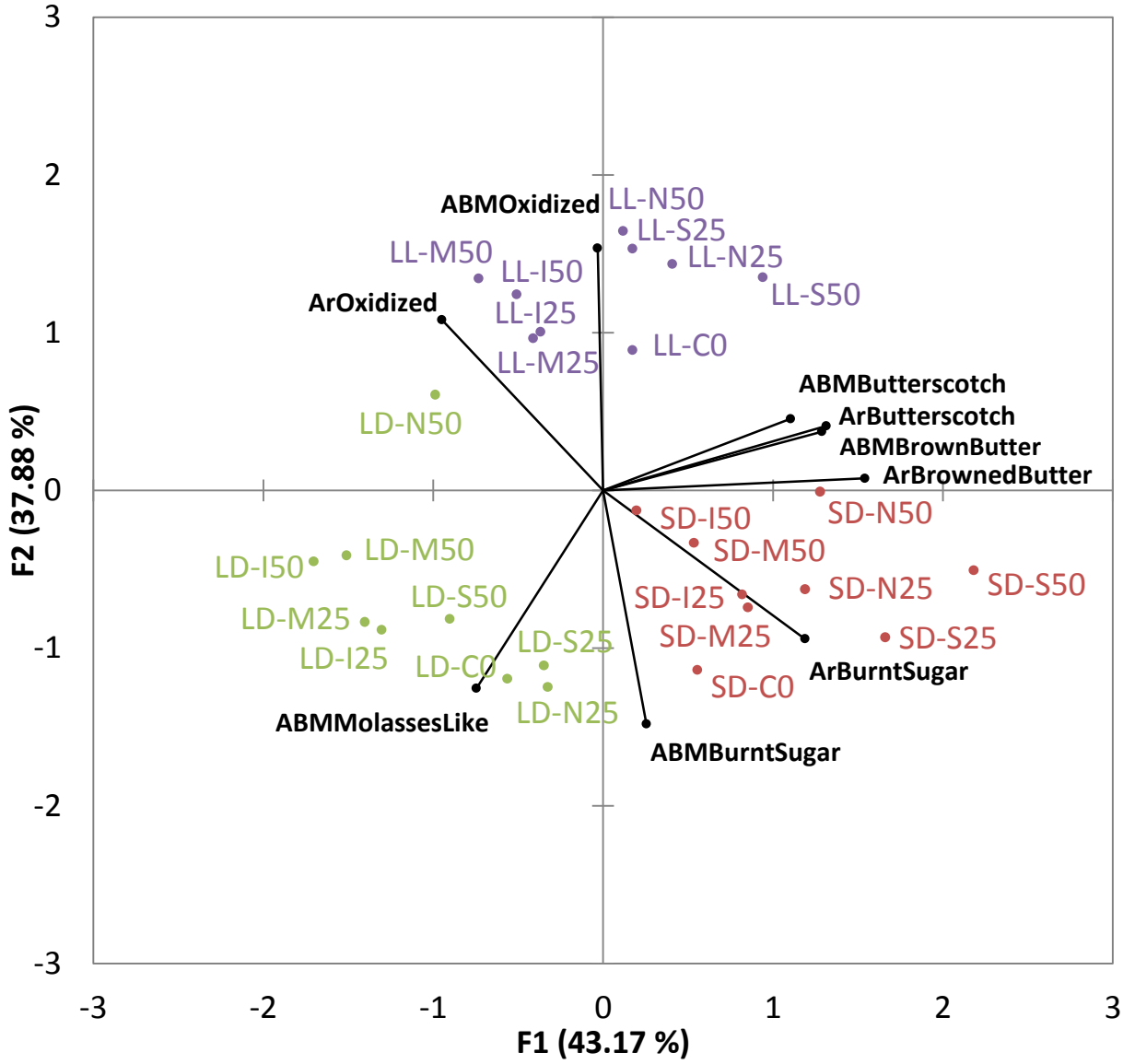

Figure 4.3. Principal Component Analysis Pearson correlation biplot with Varimax rotation of caramel coating samples by Aroma (denoted by prefix Ar) and Aroma-by mouth (denoted by prefix ABM) sensory attributes. SD stands for small-scale dark (shown in red); LD stands for large-scale dark (shown in green); LL stands for large-scale light (shown in purple); C0 stands for full-sugar control; I stands for isomalt; M stands for maltitol; N stands for mannitol; S stands for sorbitol; 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol.

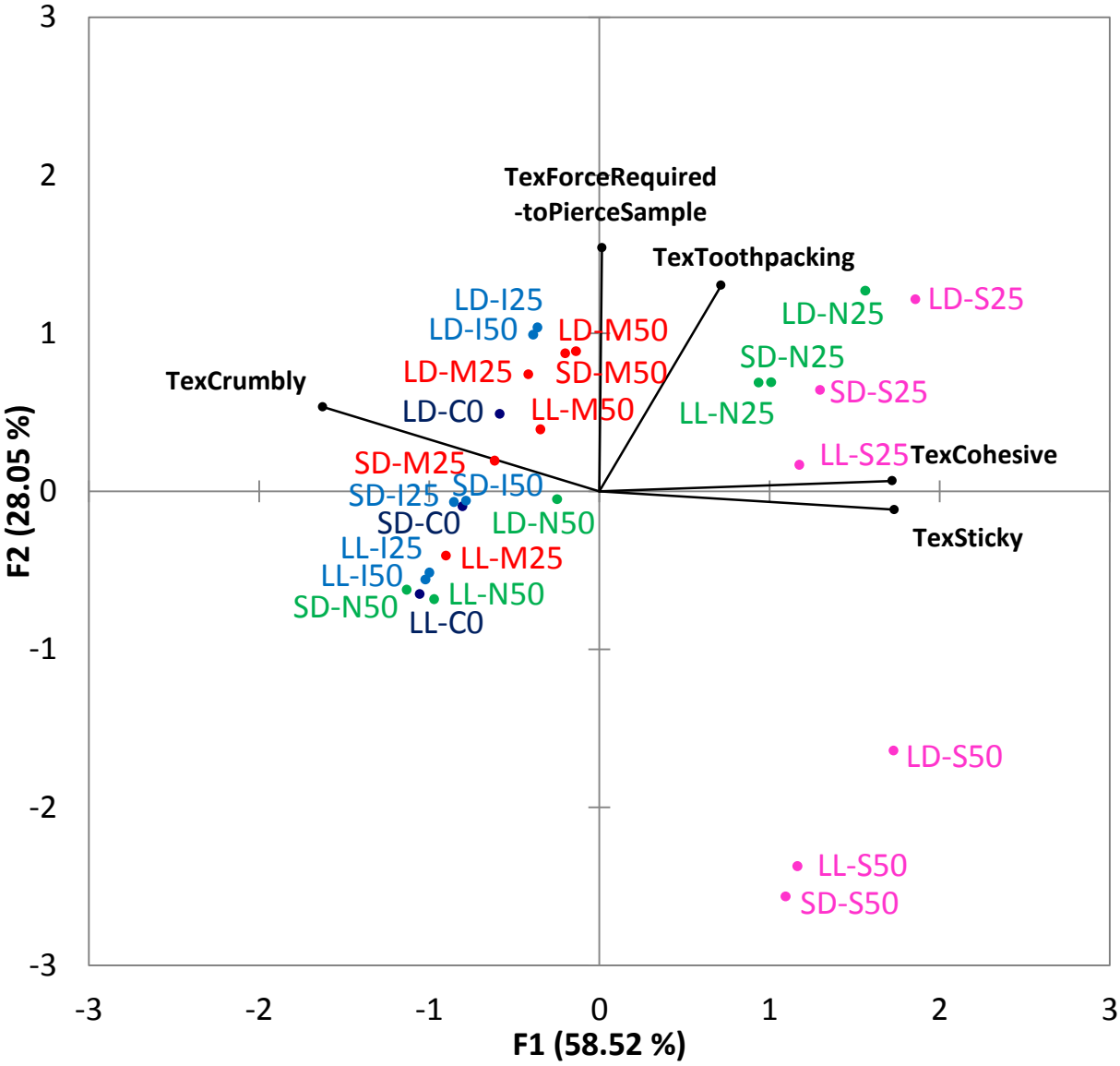

Figure 4.4. Principal Component Analysis Pearson correlation biplot with Varimax rotation of caramel coating system samples by Texture (denoted by prefix Tex) sensory attributes. SD stands for small-scale dark; LD stands for large-scale dark; LL stands for large-scale light; C0 stands for full-sugar control (shown in navy blue); I stands for isomalt (shown in blue); M stands for maltitol (shown in red); N stands for mannitol (shown in green); S stands for sorbitol (shown in pink); 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol.

Table 4.1. Ingredient quantities for full-sugar, 25% reduced sugar, and 50% reduced sugar batches of small-scale dark, large-scale dark, and large-scale light caramel formulations. Sugar contribution from corn syrup was calculated from the percent sugars by weight (50%) of the corn syrup; sugar contributors and replacers are in bold.

Formula:	**Small-Scale Dark**			**Large-Scale Dark**			**Large-Scale Light**		
Sugar Level:	**Full Sugar**	**25% Reduced**	**50% Reduced**	**Full Sugar**	**25% Reduced**	**50% Reduced**	**Full Sugar**	**25% Reduced**	**50% Reduced**
Ingredient	Quantity (g)			Quantity (g)			Quantity (g)		
Brown sugar	**240**	**168.75**	**97.5**	**245**	**158.75**	**72.5**	**0**	**0**	**0**
Sugar	**0**	**0**	**0**	**0**	**0**	**0**	**145**	**90**	**35**
Corn syrup	90	90	90	200	200	200	150	150	150
Sugar alcohol	**0**	**71.25**	**142.5**	**0**	**86.25**	**172.5**	**0**	**55**	**110**
Butter	140	140	140	0	0	0	125	125	125
Corn oil	**0**	**0**	**0**	50	50	50	0	0	0
Soybean oil	0	0	0	0	0	0	75	75	75
Water	25	25	25	0	0	0	0	0	0
Salt	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Baking soda	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Total mass:	500	500	500	500	500	500	500	500	500
Total sugar:	285	213.75	142.5	345	258.75	172.5	220	165	110
Total sugar alcohol:	0	71.25	142.5	0	86.25	172.5	0	55	110

Table 4.2. Manufacturer or distributer information for all ingredients used in production of caramel coating model systems.

Ingredient	**Manufacturer or Distributer**
Dark brown cane sugar	Domino Foods, Inc., Yonkers, NY
Beet sugar	Meijer Distribution, Inc., Grand Rapids, MI
Corn syrup (DE 60-67)	Gordon Food Service, Grand Rapids, MI
Butter	Land-O-Lakes, Inc., Arden Hills, MN
Corn oil Soybean oil	Crisco, Manufactured by the J.M. Smucker Company, Orrville, OH
Purified water	Dasani, The Coca-Cola Company, Atlanta, GA
Salt	Morton Salt, Inc., Chicago, IL
Baking soda	Arm & Hammer, Division of Church & Dwight Co., Inc., Princeton, NJ
Isomalt	CK Products, LLC, Fort Wayne, IN
Maltitol Mannitol Sorbitol	Manufacturer requests nondisclosure

Table 4.3. Complete list of sensory attributes used in descriptive analysis test with corresponding references, definitions, procedures for sample and reference evaluations, and reference ratings on a scale of 0 to 15, grouped by sensory modality.

Modality	Attribute	Reference	Definition	Procedure for Sample	Procedure for Reference	Reference Rating
Appearance	Glossy	Natural Peanut Butter	Reflective of light on surface	Lid off, Evaluate one cube at random, Choose the side with the greatest intensity for that attribute	Lid off, Move cup around, look at center of cup	**14**
	Porous	Picture of Taffy	Containing small holes or crevices on surface		Look at whole picture, evaluate density of pores (number and size)	**8**
	Bubbled	Picture of Ice Cube	Containing small air pockets just below surface		Look at lower left corner of picture, evaluate density of bubbles (just number)	**11**
	Darkness	Paint Swatch - Greyscale	The value of the sample		Evaluate over white paper, Use 2nd, 3rd & 4th color as weighted references	**4 – 7 – 12**
Aroma	Browned Butter	Browned Butter	Aroma of caramelized butter	Shake caramel samples, Crack the corner of the lid, Bunny sniff	Crack the corner of the lid, Bunny sniff	**13**
	Burnt Sugar	Toasted Marshmallow	Aroma of burnt sugar			**12**
	Oxidized	Crisco	Aroma of rancid oil			**12**
	Butterscotch	Butterscotch Topping	Sweet dairy aroma		Remove lid, Let reference air for 3 seconds, place cup over nose and smell	**12**
Texture	Toothpacking	Lifesaver (pineapple)	Packs into back teeth (at any point while chewing)	Chew thoroughly with back teeth	Break off piece with teeth and chew thoroughly	**12**
	Crumbly	Peanut Butter Bar	Readily breaks into little pieces under pressure	Chew 3 times with back teeth	Take small bite and chew 3 times with back teeth	**12**
	Sticky	Milk Duds	Sample sticks to teeth	Chew thoroughly with back teeth	Chew 1 piece thoroughly with back teeth	**9**
	Cohesive	Mamba	Sample sticks to itself throughout chewing process		Bite off 1/3 of bar and chew thoroughly with back teeth	**15**
	Force Required to Pierce Sample	Lifesaver (pineapple)	Initial force required to break sample	First bite with back teeth	First bite with back teeth	**12**

Table 4.3 (cont.)

Modality	Attribute	Reference	Definition	Procedure for Sample	Procedure for Reference	Reference Rating
Aroma By Mouth	Browned Butter	Browned Butter	Aroma-by-mouth of cooked butter	Choose one cube at random, Chew thoroughly with back teeth, Expectorate	Scoop up 1/2-pea-sized amount on tip of spoon, Spread on tongue, Move around	**11**
	Burnt Sugar	Burnt Sugar	Aroma-by-mouth of burnt sugar		Break off small piece (< 1 cm^2), Chew with back teeth	**12**
	Oxidized	Crisco	Aroma-by-mouth of rancid oil		Scoop up 1/2-pea-sized amount on tip of spoon, Spread on tongue, Move around	**13**
	Molasses-like	Golden Syrup	Aroma-by-mouth of molasses			**12**
	Butterscotch	Butterscotch Topping	Sweet dairy aroma-by-mouth			**12**
Taste	Sweet	3% Sucrose Solution	Sweet taste of sugar solution	Chew thoroughly with back teeth	Take small sip, swish around mouth	**9**
	Salty	0.06% NaCl Solution	Salty taste of NaCl solution			**9**
Aftertaste	Sweet	3% Sucrose Solution	Sweet aftertaste of sugar solution	Suck on sample for 5 seconds, then expectorate	Take small sip, swish around mouth, evaluate while in mouth	**10**
	Burnt Sugar	Burnt Sugar	Aftertaste of burnt sugar		Suck on small piece of sugar glass, evaluate 3 seconds after expectoration	**11**
	Cooked Dairy	Browned Butter	Aftertaste of cooked butter		Scoop up 1/2-pea-sized amount on tip of spoon, Spread on tongue, Move around, evaluate 3 seconds after expectoration	**13**
	Oily Mouthcoating	Coconut Oil	Leaves residual oily film in mouth			**12**

Table 4.4. Sensory attribute mean ratings from descriptive analysis test for each formula type and attribute Least Significant Difference (LSD) values, grouped by sensory modality. All samples from each formula type were aggregated to produce mean values for the three formula types. Ratings in the same row with the same superscript letter are not significantly different from one another at an $\alpha = 0.05$ significance level.

Modality	Attribute	Mean Rating			LSD
		SD*	LD*	LL*	
Appearance	Glossy	8.77^{C}	11.90^{A}	9.72^{B}	0.29
	Porous	7.43^{AB}	7.19^{B}	7.84^{A}	0.43
	Bubbled	5.54^{B}	12.27^{A}	3.79^{C}	0.28
	Darkness	10.61^{A}	8.16^{B}	5.78^{C}	0.18
Aroma	Browned Butter	9.16^{A}	5.58^{C}	7.35^{B}	0.33
	Burnt Sugar	7.78^{A}	5.35^{B}	4.24^{C}	0.31
	Oxidized	5.83^{C}	7.21^{B}	8.32^{A}	0.35
	Butterscotch	7.58^{A}	5.66^{C}	7.14^{B}	0.34
Texture	Toothpacking	9.89^{B}	11.31^{A}	9.51^{C}	0.31
	Crumbly	7.79^{B}	6.42^{C}	8.28^{A}	0.24
	Sticky	6.32^{B}	7.37^{A}	6.18^{B}	0.25
	Cohesive	6.93^{B}	7.70^{A}	6.56^{C}	0.27
	Force Required to Pierce Sample	8.88^{B}	9.99^{A}	7.90^{C}	0.29
Aroma By Mouth	Browned Butter	9.25^{A}	5.07^{C}	8.39^{B}	0.27
	Burnt Sugar	9.79^{A}	8.61^{B}	4.72^{C}	0.33
	Oxidized	4.79^{B}	4.91^{B}	7.99^{A}	0.33
	Molasses-like	7.25^{B}	10.31^{A}	5.83^{C}	0.29
	Butterscotch	9.05^{A}	6.65^{B}	8.98^{A}	0.29
Taste	Sweet	9.52^{B}	10.18^{A}	8.59^{C}	0.26
	Salty	7.16^{A}	5.69^{B}	6.98^{A}	0.29
Aftertaste	Sweet	7.53^{B}	8.43^{A}	6.68^{C}	0.29
	Burnt Sugar	7.51^{A}	7.41^{A}	3.90^{B}	0.30
	Cooked Dairy	8.91^{A}	5.42^{C}	8.19^{B}	0.31
	Oily mouthcoating	5.58^{C}	6.11^{B}	7.29^{A}	0.31

*SD stands for small-scale dark; LD stands for large-scale dark; LL stands for large-scale light

Table 4.5. Sensory attribute mean ratings from descriptive analysis test for each sugar replacer and replacement level and attribute Least Significant Difference (LSD) values, grouped by sensory modality. All samples using the same sugar replacer and replacement level were aggregated to produce mean values for each sugar replacement treatment. Ratings in the same row with the same superscript letter are not significantly different from one another at an $\alpha = 0.05$ significance level.

Modality	Attribute	Mean Rating									LSD
		C0*	I25*	I50*	M25*	M50*	N25*	N50*	S25*	S50*	
Appearance	Glossy	8.78^{F}	9.43^{E}	9.58^{E}	9.83^{E}	10.43^{D}	11.18^{C}	6.18^{G}	11.87^{B}	13.89^{A}	0.50
	Porous	8.94^{A}	8.82^{A}	8.98^{A}	8.62^{A}	8.62^{A}	8.34^{A}	5.58^{C}	6.65^{B}	2.81^{D}	0.74
	Bubbled	7.76^{A}	7.62^{A}	7.95^{A}	7.72^{A}	7.64^{A}	7.54^{A}	6.57^{B}	6.62^{B}	5.37^{C}	0.48
	Darkness	9.62^{A}	8.53^{C}	6.42^{E}	9.07^{B}	6.48^{DE}	9.10^{B}	6.79^{D}	9.31^{AB}	8.32^{C}	0.32
Aroma	Browned Butter	7.47^{C}	6.31^{DE}	5.90^{E}	6.67^{D}	6.04^{E}	8.02^{BC}	8.63^{A}	8.48^{AB}	8.78^{A}	0.57
	Burnt Sugar	6.55^{A}	5.15^{C}	4.28^{D}	5.26^{C}	4.49^{D}	6.62^{A}	5.99^{B}	6.98^{A}	6.79^{A}	0.53
	Oxidized	6.98^{B}	7.08^{B}	7.88^{A}	7.72^{A}	7.69^{A}	6.29^{C}	6.98^{B}	6.63^{BC}	6.85^{BC}	0.61
	Butterscotch	6.19^{C}	5.92^{CD}	5.57^{D}	5.78^{CD}	5.64^{CD}	7.69^{B}	8.16^{AB}	7.86^{AB}	8.33^{A}	0.59
Texture	Toothpacking	9.85^{C}	10.42^{B}	10.42^{B}	10.44^{B}	11.24^{A}	11.46^{A}	7.78^{D}	11.20^{A}	9.32^{C}	0.54
	Crumbly	11.00^{A}	10.87^{A}	10.68^{A}	10.12^{B}	8.84^{C}	4.97^{E}	7.71^{D}	3.20^{F}	0.08^{G}	0.42
	Sticky	4.17^{D}	4.41^{D}	4.22^{D}	4.43^{D}	5.63^{C}	10.46^{B}	3.70^{E}	11.31^{A}	11.30^{A}	0.43
	Cohesive	4.52^{F}	4.62^{EF}	4.73^{EF}	4.90^{EF}	5.97^{D}	11.38^{B}	5.06^{E}	12.02^{A}	10.35^{C}	0.47
	Force Required to Pierce	8.23^{D}	8.38^{D}	8.29^{D}	8.65^{D}	10.23^{C}	11.79^{A}	10.82^{B}	11.75^{A}	2.18^{E}	0.51
Aroma By Mouth	Browned Butter	8.34^{A}	7.72^{BCD}	7.32^{D}	7.73^{BCD}	7.29^{D}	7.59^{CD}	6.14^{E}	7.88^{ABC}	8.12^{AB}	0.47
	Burnt Sugar	9.75^{A}	8.34^{C}	7.14^{E}	9.07^{B}	7.26^{E}	7.49^{ED}	5.03^{F}	7.98^{CD}	7.30^{E}	0.57
	Oxidized	5.42^{CD}	5.42^{BCD}	5.90^{BC}	5.27^{D}	5.98^{B}	5.58^{BCD}	7.88^{A}	5.79^{BCD}	5.82^{BCD}	0.56
	Molasses-like	8.59^{A}	8.36^{AB}	7.71^{C}	8.43^{A}	7.63^{C}	7.52^{C}	5.37^{D}	7.90^{BC}	8.67^{A}	0.50
	Butterscotch	7.91^{CD}	8.51^{B}	7.86^{D}	8.47^{B}	8.09^{BCD}	8.38^{BC}	6.61^{E}	8.20^{BCD}	10.02^{A}	0.50
Taste	Sweet	9.78^{BC}	9.81^{B}	9.05^{D}	9.94^{B}	9.34^{CD}	9.32^{D}	7.68^{E}	9.32^{D}	10.62^{A}	0.45
	Salty	7.38^{A}	6.68^{BC}	6.82^{BC}	6.75^{BC}	6.52^{C}	6.52^{C}	5.18^{D}	6.56^{BC}	7.07^{AB}	0.51
Aftertaste	Sweet	8.15^{AB}	7.76^{BC}	6.55^{D}	8.16^{AB}	7.38^{C}	8.26^{AB}	4.63^{E}	8.48^{A}	8.57^{A}	0.50
	Burnt Sugar	7.92^{A}	6.61^{BC}	5.38^{E}	6.97^{B}	5.73^{ED}	6.89^{B}	3.79^{F}	7.00^{B}	6.19^{CD}	0.52
	Cooked Dairy	8.12^{A}	7.56^{BCD}	7.09^{D}	7.92^{ABC}	7.42^{CD}	8.09^{AB}	4.84^{E}	8.29^{A}	8.22^{A}	0.54
	Oily mouthcoating	5.77^{C}	6.08^{BC}	6.47^{B}	6.42^{B}	6.50^{B}	6.07^{BC}	4.16^{D}	6.38^{B}	9.06^{A}	0.54

*C0 stands for full-sugar control; I stands for isomalt; M stands for maltitol; N stands for mannitol; S stands for sorbitol; 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol

Table 4.6. Water activity (a_w), moisture content expressed in percent wet basis (% wb), onset, midpoint, and endpoint temperatures of the glass transition (T_g), and onset temperature of melting (T_m) of caramel coating samples. Values in the same column and within the same formula type with the same superscript letter are not significantly different from one another at an $\alpha = 0.05$ significance level.

Sample*	a_w	Moisture Content, % wb	T_g onset (°C)	T_g midpoint (°C)	T_g endpoint (°C)	T_m onset (°C)
SD-C0	0.169^{D}	0.73^{D}	42.1^{A}	43.9^{A}	45.7^{A}	n/a
SD-I25	0.176^{C}	0.67^{D}	39.1^{A}	40.6^{B}	42.4^{B}	n/a
SD-I50	0.170^{D}	0.60^{D}	39.1^{A}	41.1^{B}	43.1^{B}	n/a
SD-M25	0.174^{C}	0.59^{D}	25.6^{B}	29.8^{C}	34.0^{C}	n/a
SD-M50	0.166^{E}	0.72^{D}	23.3^{BC}	28.2^{C}	32.8^{C}	n/a
SD-N25	0.181^{B}	1.81^{A}	21.0^{C}	22.1^{E}	23.4^{E}	n/a
SD-N50	0.241^{A}	1.59^{B}	22.8^{BC}	25.0^{D}	27.4^{D}	134.0
SD-S25	0.171^{D}	1.17^{C}	6.0^{D}	15.0^{F}	19.4^{F}	n/a
SD-S50	0.180^{B}	1.26^{C}	-2.6^{E}	3.1^{G}	8.5^{G}	n/a
LD-C0	0.259^{A}	1.19^{C}	31.7^{A}	36.5^{A}	40.9^{A}	n/a
LD-I25	0.197^{C}	0.92^{C}	29.4^{B}	34.3^{B}	39.2^{B}	n/a
LD-I50	0.133^{H}	0.88^{C}	29.5^{B}	34.7^{B}	39.8^{B}	n/a
LD-M25	0.216^{B}	1.05^{C}	27.2^{C}	32.7^{C}	37.9^{C}	n/a
LD-M50	0.148^{G}	1.09^{C}	22.7^{D}	27.9^{D}	32.9^{D}	n/a
LD-N25	0.149^{G}	2.23^{A}	13.2^{E}	18.9^{E}	24.5^{E}	n/a
LD-N50	0.176^{E}	2.14^{AB}	7.8^{F}	14.0^{F}	20.1^{F}	129.3
LD-S25	0.170^{F}	1.84^{B}	7.1^{G}	13.5^{F}	19.7^{F}	n/a
LD-S50	0.191^{D}	1.86^{B}	-4.3^{H}	0.3^{G}	4.8^{G}	n/a
LL-C0	0.142^{E}	0.60^{D}	40.6^{A}	42.4^{A}	44.1^{A}	n/a
LL-I25	0.131^{F}	0.61^{D}	39.2^{B}	41.1^{B}	43.0^{B}	n/a
LL-I50	0.201^{C}	0.59^{D}	39.0^{B}	41.2^{B}	43.4^{AB}	n/a
LL-M25	0.143^{E}	0.58^{D}	24.7^{D}	28.4^{D}	32.2^{C}	n/a
LL-M50	0.159^{D}	0.72^{CD}	28.4^{C}	30.6^{C}	32.7^{C}	n/a
LL-N25	0.155^{D}	1.43^{A}	5.7^{E}	7.2^{E}	8.7^{E}	n/a
LL-N50	0.224^{B}	1.52^{A}	5.9^{E}	8.1^{E}	10.2^{D}	119.3
LL-S25	0.155^{D}	0.84^{C}	5.8^{E}	7.4^{E}	9.1^{E}	n/a
LL-S50	0.249^{A}	1.16^{B}	-1.9^{F}	2.6^{F}	6.9^{F}	n/a

*SD stands for small-scale dark; LD stands for large-scale dark; LL stands for large-scale light; C0 stands for full-sugar control; I stands for isomalt; M stands for maltitol; N stands for mannitol; S stands for sorbitol; 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol

Table 4.7. Thermal properties of carbohydrate ingredients, including the average onset temperature of melting (T_m) on the first heating, onset, midpoint, and endpoint temperatures of the glass transition (T_g), and change in specific heat at the glass transition (Δc_p) values determined experimentally for sucrose, brown sugar, corn syrup, isomalt, maltitol, mannitol and sorbitol.

Ingredient	**T_m onset (°C)**	**T_g onset (°C)**	**T_g midpoint (°C)**	**T_g endpoint (°C)**	**Δc_p (J/g/°C)**
Sucrose	188.5	67.1	70.5	73.6	0.71
Brown sugar	170.5	41.6	46.8	51.8	0.73
Corn syrup	not present	-62.3	-55.8	-49.5	0.82
Isomalt	133.9	38.7	43.2	47.3	0.96
Maltitol	138.4	35.9	40.0	43.9	0.74
Mannitol	165.7	not present			
Sorbitol	95.1	-7.9	-4.6	-1.9	1.16

Table 4.8. Average values for Texture Profile Analysis parameters of fracturability, hardness, springiness, chewiness, resilience, cohesiveness, and adhesiveness. Values in the same column and within the same formula type with the same superscript letter are not significantly different from one another at an $\alpha = 0.05$ significance level.

Sample*	Fracturability	Hardness	Springiness	Chewiness	Resilience	Cohesiveness	Adhesiveness
SD-C0	0.75^{B}	90.03^{D}	0.75^{B}	57.68^{B}	0.72^{B}	0.73^{B}	4.22^{C}
SD-I25	3.80^{B}	104.8^{CD}	0.91^{A}	93.02^{B}	0.91^{A}	0.96^{A}	3.72^{C}
SD-I50	2.32^{B}	96.49^{D}	0.88^{A}	81.73^{B}	0.91^{A}	0.95^{A}	0.00^{C}
SD-M25	17.29^{B}	223.5^{B}	0.93^{A}	197.7^{A}	0.93^{A}	0.96^{A}	0.00^{C}
SD-M50	46.80^{A}	268.3^{A}	0.72^{B}	194.6^{A}	0.76^{B}	0.82^{B}	0.00^{C}
SD-N25	16.10^{B}	140.2^{C}	0.53^{C}	61.25^{B}	0.49^{C}	0.53^{C}	29.37^{BC}
SD-N50	0.03^{B}	39.37^{E}	0.53^{C}	11.29^{C}	0.34^{D}	0.51^{C}	5.10^{C}
SD-S25	0.00^{B}	25.10^{E}	0.38^{D}	3.13^{C}	0.25^{E}	0.29^{D}	285.1^{A}
SD-S50	0.00^{B}	1.71^{E}	0.73^{B}	0.50^{C}	0.10^{F}	0.46^{C}	66.06^{B}
LD-C0	13.07^{A}	218.9^{B}	0.56^{BC}	107.2^{A}	0.61^{AB}	0.60^{B}	19.35^{C}
LD-I25	0.00^{B}	111.7^{C}	0.56^{BC}	56.40^{BC}	0.57^{ABC}	0.57^{B}	0.42^{C}
LD-I50	3.02^{B}	77.20^{C}	0.65^{B}	45.72^{CD}	0.67^{A}	0.68^{AB}	3.95^{C}
LD-M25	0.00^{B}	68.20^{CD}	0.52^{BC}	29.90^{CDE}	0.63^{A}	0.66^{AB}	10.61^{C}
LD-M50	3.98^{AB}	290.6^{A}	0.59^{BC}	98.76^{AB}	0.48^{BCD}	0.56^{BC}	566.2^{A}
LD-N25	0.00^{B}	256.2^{AB}	0.46^{CD}	49.57^{C}	0.40^{D}	0.40^{CD}	148.7^{BC}
LD-N50	0.00^{B}	105.0^{C}	0.56^{BC}	39.93^{CDE}	0.45^{CD}	0.58^{B}	2.42^{C}
LD-S25	0.00^{B}	17.02^{DE}	0.31^{D}	1.63^{E}	0.19^{E}	0.26^{D}	260.2^{B}
LD-S50	0.00^{B}	0.50^{E}	0.98^{A}	0.38^{E}	0.08^{E}	0.78^{A}	112.9^{BC}
LL-C0	1.84^{A}	72.57^{CD}	0.59^{C}	25.90^{CD}	0.56^{AB}	0.54^{BC}	9.96^{C}
LL-I25	0.00^{A}	90.10^{C}	0.58^{C}	29.00^{BCD}	0.55^{BC}	0.53^{BC}	13.09^{C}
LL-I50	0.00^{A}	160.2^{B}	0.53^{C}	44.64^{B}	0.50^{C}	0.51^{C}	4.91^{C}
LL-M25	5.06^{A}	52.18^{DE}	0.41^{D}	14.01^{DE}	0.34^{D}	0.38^{D}	22.39^{C}
LL-M50	0.00^{A}	284.6^{A}	0.66^{B}	125.1^{A}	0.61^{A}	0.60^{AB}	105.2^{B}
LL-N25	0.00^{A}	152.9^{B}	0.46^{D}	34.81^{BC}	0.35^{D}	0.44^{D}	4.68^{C}
LL-N50	0.00^{A}	49.51^{E}	0.53^{C}	14.96^{DE}	0.35^{D}	0.52^{C}	2.50^{C}
LL-S25	0.00^{A}	16.04^{F}	0.23^{E}	1.06^{E}	0.13^{E}	0.20^{E}	89.46^{B}
LL-S50	0.00^{A}	1.13^{F}	0.93^{A}	0.73^{E}	0.06^{F}	0.65^{A}	177.8^{A}

*SD stands for small-scale dark; LD stands for large-scale dark; LL stands for large-scale light; C0 stands for full-sugar control; I stands for isomalt; M stands for maltitol; N stands for mannitol; S stands for sorbitol; 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol

Table 4.9. Pearson's correlation matrix of sensory texture properties evaluated by the descriptive analysis panel, moisture content, water activity (a_w), thermal properties related to the glass transition temperature (T_g) and change in specific heat (Δc_p), and textural properties calculated from texture profile analysis data of the samples. Pearson's correlation coefficients in bold are different from 0 with a significance level of $\alpha = 0.05$

Measurement Type	Variable	Sensory Textural Properties				
		Force Required to Pierce Sample	Crumbly	Sticky	Cohesive	Toothpacking
Sensory Textural Properties	Force Required to Pierce Sample	**1**	0.186	-0.078	0.113	**0.371**
	Crumbly	0.186	**1**	**-0.888**	**-0.877**	-0.089
	Sticky	-0.078	**-0.888**	**1**	**0.937**	**0.361**
	Cohesive	0.113	**-0.877**	**0.937**	**1**	**0.326**
	Toothpacking	**0.371**	-0.089	**0.361**	**0.326**	**1**
Water-Related Properties	Average moisture content	0.264	**-0.651**	**0.547**	**0.581**	0.071
	Average a_w	-0.172	-0.113	-0.037	-0.060	-0.242
Thermal Properties	T_g onset	0.104	**0.900**	**-0.740**	**-0.757**	0.036
	T_g midpoint	0.131	**0.885**	**-0.733**	**-0.747**	0.090
	T_g endpoint	0.144	**0.859**	**-0.722**	**-0.738**	0.136
	Δc_p	-0.170	**-0.461**	**0.375**	**0.326**	**0.372**
Texture Profile Analysis Properties	Fracturability	0.015	0.118	-0.093	-0.093	-0.047
	Hardness	**0.365**	**0.350**	-0.219	-0.200	**0.378**
	Springiness	**-0.367**	-0.255	0.121	0.125	-0.140
	Chewiness	0.152	**0.403**	**-0.338**	**-0.338**	0.233
	Resilience	0.239	**0.758**	**-0.640**	**-0.618**	0.187
	Cohesiveness	-0.090	0.137	-0.108	-0.121	0.031
	Adhesiveness	0.155	**-0.391**	**0.408**	**0.394**	0.250

Chapter 5: Correlation of consumer perception of stickiness and contributing texture attributes to trained panelist evaluations in a caramel system

5.1 Abstract

Stickiness is a critical, but complex attribute with relevance to many food systems. Consumer perception of stickiness is subjective and variable; however, stickiness ratings and texture insights from trained panels are often used to make decisions about consumer products. Our objectives were to correlate trained panel evaluations to consumer perception of stickiness and to identify texture attributes that contribute to stickiness. Nine diverse caramel samples were assessed by two panels. First, trained panelists participated in texture term generation, temporal dominance of sensation (TDS), and tactile and oral stickiness intensity rating. Next, 75 consumers participated in a two-part test: first, they completed a check-all-that-apply (CATA) exercise with the TDS panel-generated terms; second, they scored each sample for overall tactile and oral stickiness intensity. Trained panelist and consumer stickiness ratings were then correlated to each other and to TDS parameters for each attribute. Consumers and trained panelists showed good agreement in tactile ($r=0.86$, $p<0.01$) and oral ($r=0.94$, $p<0.001$) stickiness ratings. Samples presenting high levels of tacky, stringy, and enveloping attributes were rated the stickiest. A subset of attributes, including toothpacking and deformable, correlated positively with stickiness when multiple selections were permitted (CATA) and negatively when only one selection was permitted (TDS), illuminating a hierarchy in stickiness-contributing attributes. The presence of toothpacking and deformable textures increased stickiness perception, but less so than tacky, stringy, and enveloping textures.

Identification of texture factors that most strongly relate to consumer perception of stickiness will enable informed testing of stickiness properties and formulation of sticky products.

5.2 Introduction

The prevalent application of trained panelist data to explaining or predicting consumer preferences and perceptions has sparked an interest in the relevance of trained panel data to the consumer experience, as well as in the ability of consumers to provide robust descriptive data. To test the degree to which consumer profiling agrees with the traditionally valued trained panelist profile data, researchers have implemented and analyzed a wide variety of test methods and metrics to compare consumer and trained sensory data (Gómez and others 1998; Hersleth and others 2005; Worch and others 2010; Ares and others 2015). Conclusions concerning the relative validity of descriptive consumer data have differed depending on products and attributes tested, sensory testing and data analysis methodologies used, and researcher perspective on acceptable variability. Product complexity has also been cited as a key factor in determining the ability of consumers to generate consistent and meaningful sensory data, as consumers may show less agreement with trained panelists when asked to assess more complex products or attributes (Ares and others 2015).

A prevalent and impactful complex sensory attribute, sticky texture has been the subject of much research and discussion, but little consensus (Kilcast and Roberts 1998). Stickiness of foods has often been associated with dental adhesion; however, previous research has shown a lack of correlation between perceived stickiness and degree of food retention on oral surfaces (Kashket and others 1991). Stickiness has been studied and quantified in numerous sensory

panels, in which the definitions and reference samples used to describe sticky texture differ as widely as the products assessed. This variation is due to the impact of food context on the meaning of stickiness: stickiness in cream cheese has been defined as the "amount of sample that adheres to the palate" (Brighenti and others 2008), while in rice it has been defined as the "degree to which the grains adhere together" (Rousset and others 1999).

In addition to the strong influence of food context, the understanding and assessment of sticky texture in foods is also challenged by the multifaceted nature of stickiness. Sticky texture has been attributed to a combination of a variety of factors, including adhesiveness, cohesiveness, viscosity, chewiness, and moisture content (Caldwell 1970; Adhikari and others 2001). The degree to which these and other factors influence total stickiness perception is not yet well understood. Even the most straightforward facet of stickiness, surface adhesiveness, is not simple to evaluate via a single measurement, as people use a variety of processes and body surfaces to interact with and assess foods, including touching or chewing with hands, tongue, teeth, and other oral surfaces (Jowitt 1974; Adhikari and others 2001).

Nonetheless, stickiness is frequently measured both instrumentally and by sensory panels (Chung and others 1999; Rousset and others 1999; Steiner and others 2003; Brighenti and others 2008; Silalai and Roos 2011). Descriptive methodologies, such as Spectrum and Quantitative Descriptive Analysis (QDA), are commonly used to measure sensory stickiness, but these methods may introduce bias or reduce the dimensionality in the assessment of stickiness through use of a narrow definition or specific reference product during training. As a result of this focused training, the quantification of sample stickiness may instead be a quantification of

the degree to which the stickiness of the sample resembles that of the reference product or the degree to which it fits the given definition of stickiness.

In this study, a diverse group of sensory methods were selected in order to maximize the amount of information gathered on stickiness and sample texture, while minimizing the bias and restrictions placed on panelists when assessing the overall stickiness of samples. Texture attributes were assessed both cumulatively, i.e., evaluated as perceived in total during mastication, through the Check-All-That-Apply (CATA) method, and temporally, i.e., assessed dynamically over time throughout the mastication process, using the Temporal Dominance of Sensations (TDS) method (Pineau and others 2003; Pineau and others 2009). Caramel samples formulated to present a diverse range of textures were utilized in this study. Many types of food components and products may be categorized as caramel; in this case, a model system analogous to the caramel coating used in caramel popcorn products and composed primarily of sugars and lipids was used. Caramel samples provide a logical model system due to the importance of stickiness to signature caramel texture and the importance of texture to appreciation of caramel products (Steiner and others 2003; Mendenhall and Hartel 2014). The importance of stickiness and texture to consumers in caramel products underscores the importance of validating the relevance of trained panelist data to consumer perception of stickiness.

The first objective of this study was to relate consumer and trained panelist perceptions of stickiness in a caramel system. We hypothesized that consumers and trained panelists would agree in stickiness rating trends but would differ in scale usage. In order to deepen

understanding and articulation of the texture facets of stickiness in foods, the second objective of this study was to identify texture attributes that contribute to stickiness perception. We hypothesized that stickiness would be positively influenced by multiple texture attributes related to the cohesive and adhesive properties of the material.

5.3 Materials and methods

Caramel preparation

In a previous study, caramel popcorn products were characterized and categorized into three dominant categories, from which three caramel coating model systems were developed (Mayhew and others 2016). This study utilizes one of the three model systems, the "Large-scale Dark" formula, so named because of the large-scale production and national distribution and the dark color and flavor profile of the products comprising the category. The formula of the Large-scale Dark model system is described in Table 5.1. Control full-sugar batches were formulated with brown sugar and corn syrup, while reduced sugar batches replaced 25 or 50% of the total sugar with one of four sugar alcohols: isomalt, maltitol, mannitol, or sorbitol. The mass of the total sugar was calculated as the sum of the mass of brown sugar and the mass of sugars contributed by the corn syrup; however, only brown sugar was replaced by sugar alcohols in the reduced sugar formulas in order to maintain a consistent concentration of the non-sugar components of corn syrup. Samples were coded to designate the formula type, sugar replacer, and sugar replacement level. The sugar replacer codes include C for control, or no sugar replacer, I for isomalt, M for maltitol, N for mannitol, and S for sorbitol. Sugar replacement levels are indicated by the number of the percent replacement: 0 for 0% sugar replacement, 25 for 25% sugar replacement, and 50 for 50% sugar replacement. In the

production of each sample, all ingredients except for baking soda were added to a stainless steel pan and stirred constantly while heated on a gas range to a final temperature of 150°C, which corresponds to the "hard crack" stage of sugar cooking. Throughout the cooking process, the temperature was monitored with a high accuracy Traceable® thermocouple (Thermo Fisher Scientific Company, Waltham, Massachusetts, U.S.A.). After the final temperature was achieved, baking soda was whisked in for 15 s, samples were poured into silicon molds (WOOTOP, Shenzhen, Guangdon, China), covered with aluminum foil, and allowed to cool at 22°C. Resultant 1.0 cm^3 caramel sample cubes were then vacuum sealed and stored in an opaque and lidded tub to limit changes in sample moisture content and minimize lipid oxidation. One batch of each sample was produced for Temporal Dominance of Sensation (TDS) panel training, while a second batch was produced for both TDS and consumer test data collection.

Temporal dominance of sensation testing

Forty-one panelists were recruited to participate in a two-part screening procedure, administered using Qualtrics (Qualtrics, Provo, UT, U.S.A.), screening panelists for subjects with good oral health, non-smoking status, lack of prohibitory food allergies, ability to discriminate between and generate meaningful texture descriptors for caramel samples, and consistent availability. Out of the 41 screened, 16 panelists (11 female, 5 male, ages 22-45 yrs.) passed the screening procedure and elected to join the Temporal Dominance of Sensation (TDS) study. Panelists met as a group for one hour each day for the first eight days of the study to receive training on descriptive and TDS methodology, to generate texture terms, definitions, and related references that described the texture of the caramel coating system samples, and to

practice selecting the most dominant texture attributes as they arose during the mastication process. During training sessions, four sample cubes (1.0 cm^3) per sample of a balanced rotation of four sample types were served in plastic 29.5 mL cups with lids (Solo Cup Company, Inc., Chicago, IL) and labeled with randomized three-digit numbers. Requested references were also served in plastic cups with lids (Solo Cup Company, Inc., Chicago, IL) and labeled with their identity. The finalized list of texture attributes, definitions, and references is provided in Table 5.2.

On days 9 and 10, panelists participated in individual practice sessions to familiarize themselves with the test procedure and software system. Sample evaluation for the TDS study occurred over two days (day 11 and 12) in three 30-minute sessions. Panelists were served one sample cube (1.0 cm^3) for each test sample in a lidded 29.5 mL cup with a random three-digit code. Panelists evaluated all nine samples in each session with a 2-minute break every third sample. Sample presentation order was randomized using a William's Latin square design and attribute display order within the test was held constant within each session, but randomized across panelists and sessions to reduce attribute selection bias. Each sample was evaluated by each panelist a total of three times for 48 total replicates per sample.

Temporal data collection was accomplished using the sensory data acquisition and analysis software TimeSens® (www.timesens.com) and occurred in environmentally controlled (22°C and 33% relative humidity) individual booths. Panelists were instructed to rinse their mouths with warm water, a bite of carrot, and room temperature water between each sample and to expectorate all samples and rinses. On days 13 and 14, panelists were trained for and

participated in the second half of the consumer test described below to provide a trained counterpoint to consumer evaluation of oral and tactile sample stickiness.

Consumer testing

Consumers were recruited to participate in a test designed to measure consumer assessment and liking of caramel texture. One-hundred-and-four potential subjects completed a screening questionnaire designed to select participants who were consumers of caramel products, non-smokers, and free of prohibitory allergies. Consumers who passed the screening survey were invited to participate in a two-day test on caramel texture comprised of two 40-minute test sessions spaced two days apart. The screening questionnaire and two-part test were both built and administered with Qualtrics survey distribution program (Qualtrics, Provo, UT, U.S.A.). For each evaluation, panelists were served one caramel sample cube (1.0 cm^3) in a 29.5 mL lidded plastic cup (Solo Cup Company, Inc., Chicago, IL) and instructed to rinse before and between evaluations with warm water, a bite of carrot, and room temperature water and to expectorate all samples and rinses. In the first session, panelists were asked to rate their liking of each of nine caramel samples on a 9-point hedonic scale, in part to familiarize panelists with the sample set.

Panelists were then asked to provide a personal definition of stickiness and list any synonyms for stickiness and examples or counterexamples of sticky materials. Finally, they were presented with a second set of the same nine samples, labeled with different codes, and asked to evaluate each sample and check all that apply (CATA) from a list of texture terms generated by the TDS panelists and described in Table 5.2. Sample presentation order and CATA

attribute order were randomized across panelists. Eighty-two panelists completed the first session of this test.

In the second session, panelists were asked to evaluate the stickiness of caramel samples first by hand, to rate tactile stickiness, and then by mouth, to rate oral stickiness. Separate sample sets with different 3-digit codes were provided for each evaluation type. In both cases, subjects were asked to score the stickiness of samples on a scale of 0 to 10, where 0 is “Not sticky at all” and 10 is “Extremely sticky”. For the tactile portion of the test, panelists were instructed to rinse their fingers between samples using a moist sponge and a paper napkin. At the end of the second session, panelists were invited to complete a brief survey on their demographical background and opinions on sugars and sugar alcohols. Seventy-five panelists completed both the first and second sessions of the test.

Statistical analysis

Hierarchical clustering of consumer stickiness ratings was conducted using the VARCLUS procedure in SAS statistical software (Version 9.2, SAS, Cary, NC, U.S.A.) with the CENTROID option to insure consumers with opposite preferences (strong negative correlations) are not clustered together. Tactile and oral stickiness ratings were included in the clustering analysis.

Pearson correlation analysis was used to relate consumer panel and trained panel scores for sample tactile and oral stickiness. Each correlation coefficient was based on the 2 vectors of 9 product means. The analysis was conducted using XLSTAT (Addinsoft, New York, NY, U.S.A.) with a significance level of $\alpha = 0.05$.

Analysis of variance (ANOVA) and means separation were performed to determine if significant differences ($\alpha = 0.05$) existed between the stickiness intensity scores elicited by samples and to identify which samples showed significant differences in stickiness scores using the proc GLM method in SAS statistical software (Version 9.2, SAS, Cary, NC, U.S.A.) with a two-way model including sample as a fixed effect and subject as a random one.

Cochran's Q test was performed using the CATA analysis program in XLSTAT (Addinsoft, New York, NY, U.S.A.) in order to identify differences ($\alpha = 0.05$) in the frequency of texture attribute selection for each sample during the CATA exercise.

Covariance principal components analysis (PCA) was conducted in XLSTAT (Addinsoft, New York, NY, U.S.A.) on the frequency of CATA term usage in order to produce a biplot depicting differences in texture term usage by consumers between caramel samples.

Extraction of TDS parameters was conducted using TimeSens® software. The temporal dominance data were time standardized across panelists at the start and end of evaluations to reduce the effect of differences in mastication rates. The duration of dominance and the maximum percent dominance rate were extracted for each attribute and product.

Hotelling canonical variates analysis (CVA) was performed to describe trends and differences between samples in the duration of dominance for the attributes measured. A CVA Hotelling table and a CVA biplot with 90% confidence ellipses for samples were generated using TimeSens®.

Spearman correlation analysis was used to evaluate the contribution of texture attributes to consumer perception and trained panelist evaluation of overall oral stickiness. The Spearman correlation program in XLSTAT (Addinsoft, New York, NY, U.S.A.) was used to relate both CATA counts and extracted TDS parameters to oral stickiness intensity ratings. A significance level of 0.05 was used to determine if correlations were statistically significant.

5.4 Results

Stickiness intensity

Caramel samples differed significantly in perceived stickiness intensity when evaluated by consumers and trained panelists both by hand (tactile) and by mouth (oral) (Table 5.3). Both panels showed reasonably low variation in rating trends, allowing for statistically significant separation of sample stickiness means. Sample F-values, and consequently the discrimination power, for tactile and oral stickiness were slightly higher for the consumer panel (n=75, $F_{tactile}$=98.08, F_{oral}=195.89) than the trained panel (n=16, $F_{tactile}$=45.69, F_{oral}=134.22). Sample S50 received the highest tactile and oral stickiness ratings from both panels, while N50 received the lowest tactile stickiness ratings from both panels. Consumers gave samples C0 and I50 the lowest oral stickiness ratings; trained panelists likewise rated these samples among the least sticky orally, in addition to sample N50. The wide spread of mean sample stickiness ratings provides a strong data set for comparison of consumer and trained panelist rating trends, as well as texture profile to stickiness rating correlations.

Clustering analysis

After centering stickiness ratings by judge, hierarchical clustering of consumer stickiness ratings revealed a lack of meaningful consumer segmentation by rating behaviors. ANOVA of centered stickiness data within hierarchical clusters showed that dividing the consumer panel into greater than one cluster resulted in a loss of power or a decrease in F (Table 5.4). This indicates that consumers generally agree in the stickiness rankings within this sample set, though they may differ in scale usage.

Correlation of consumer and trained panelist stickiness ratings

Significant positive correlations were found between consumer and trained panelist evaluations of tactile (r=0.855) and oral stickiness (r=0.937) (Table 5.5). While both correlations are indicative of strong agreement between panels, it is notable that consumers and trained panelists agreed on oral stickiness ratings to a greater extent than on tactile stickiness ratings. An inability of consumers to differentiate among samples of moderate tactile stickiness (I25, I50, M25, M50), along with conservative use of the upper end of the scale by consumers, could be responsible for the weaker correlation between tactile stickiness scores (Figure 5.1). Significant positive correlations were also identified between tactile and oral stickiness ratings of caramel samples by consumers (r=0.820), trained panelists (r=0.689), and between consumer tactile and trained panelist oral stickiness (r=0.736). These strong positive correlations suggest that samples presenting a high degree of tactile stickiness also present a high degree of oral stickiness. The weaker correlation between tactile and oral stickiness among trained panelists indicates that expert evaluators use more dissimilar criteria for evaluating tactile and oral

stickiness, while consumers are more likely to rate samples similarly whether asked to evaluate samples by hand or by mouth.

Identification of texture attributes related to stickiness

Trained panelists identified and defined eight texture terms with relevance to stickiness perception (Table 5.2). These terms were divided into three researcher-designated attribute categories: terms relating to the break versus bend behavior of samples, including brittle, crumbly, and deformable, terms relating to the adhesiveness of samples, including enveloping, tacky, and toothpacking, and terms related to the cohesiveness of samples, including cohesive. The final term, stringy, was categorized as related to both adhesive and cohesive properties.

Texture profile by TDS

Application of CVA to TDS data showed a separation of samples by the duration of dominance of each texture attribute (Figure 5.2). A high percentage of the total variation in attribute dominance was explained by the first two axes, 87.07%, while 11.07% of the variation was explained by the third axis. Ninety percent confidence ellipses generated around the mean position of each sample in the plot enable easy visualization of texture profile uncertainty and provide conservative visual separation of statistically distinct samples, relative to p-values from Hotelling pairwise sample comparisons. The x-axis captured 65.57% of the total variation in duration data and described a continuum from enveloping and stringy in the positive direction to crumbly, toothpacking, and cohesive in the negative direction. The y-axis explained 21.5% of the total variation in duration and described tacky, brittle, and toothpacking attributes in the positive direction and primarily deformable and texture in the negative direction. The third axis generally displayed a continuum from toothpacking to deformable.

Samples made with isomalt, I25 and I50, and the sample made with 50% mannitol, N50, displayed attribute duration patterns similar to that of the control, C0, described primarily by attributes loaded onto the negative x-axis: crumbly, toothpacking, and cohesive. However, according to the Hotelling pairwise comparisons, both C0 and N50 are statistically different from I25 and I50, as well as from each other (α=0.10). Differences in temporal texture profile between these samples may not be visible in Figure 5.2 because of differences in the duration of toothpacking as a dominant texture attribute between C0, N50, and I samples, which are expressed on the third CVA axis and not included in the biplot. Sample M25 resembled I25 and M50 in texture profile, though samples made with maltitol were generally dominated to a greater extent by attributes toothpacking, cohesive, and brittle relative to the control. Separated from the majority of samples, N25 and S25 presented texture profiles dominated by attributes stringy, enveloping, and tacky. The most texturally distinct sample, S50 was dominated by attributes deformable, stringy, and enveloping.

Texture profile by CATA

The frequency of attribute selection by consumers participating in the CATA study differed among products for all eight attributes ($p < 0.001$) (Table 5.6). Significantly more consumers described samples C0, I25, I50, M25, and M50 as brittle or crumbly than samples S25, and S50. This trend corresponds with the trained panelists' selection of crumbly as a dominant attribute for the same group of samples. The terms deformable, enveloping, and stringy were applied significantly more frequently to S50, and terms cohesive, tacky, and toothpacking were applied significantly more frequently to samples S50 and S25 relative to the control. Samples M50, N25 were also described as tacky significantly more frequently than the

control; samples M25, M50, and N25 were more frequently described as toothpacking than the control sample.

Although consumers were discriminating in their selection of attributes, CATA data resulted in less overall resolution than trained panelist (TDS) data. Similar samples C0, I25, I50, M25, and M50 did not differ significantly in frequency of term selection for any attribute besides toothpacking, for which sample M50 received significantly more selections than the control. Consumer data-generated sample texture profiles (Figure 5.3) also reflect a more binary characterization scheme relative to texture profiles generated from trained panel data, with 82.42% of the total variation in consumers' CATA term selection primarily dividing samples between a sticky profile (negative Factor 1) or a crumbly profile (positive Factor 1). Frequency of term selection may also have been influenced by consumers' varying degree of familiarity with the terms. Samples deemed to be the most brittle were labeled as brittle by 80% or more of the consumers, while the highest percent frequency achieved for the terms stringy and tacky were 54% and 55%, respectively.

Correlation of texture terms to stickiness intensity

Correlation of the TDS parameters maximum dominance rate and duration of dominance with trained panelist stickiness ratings, as well as correlation of the CATA frequency of term selection with consumer stickiness ratings, supports our hypothesis that cohesive and adhesive texture properties positively influence stickiness perception (Figure 5.4). Samples with a texture profile dominated by cohesive and adhesive properties enveloping, stringy, and tacky received the highest stickiness ratings from trained panelists; samples frequently identified as displaying the cohesive and adhesive attributes cohesive, enveloping, tacky, and toothpacking

received the highest stickiness ratings from consumers. The initial tendency of a caramel sample to either break or bend also influenced stickiness perception: attributes related to sample breaking, brittle and crumbly, correlated negatively to stickiness, while the attribute deformable, which describes a lack of sample breaking, correlated positively to stickiness.

Differences in the magnitude and even direction of the correlation between texture attributes and stickiness assessed by TDS or CATA point to the influence of sensory method and reveal two tiers of sticky-contributing texture attributes. TDS analysis, which allows selection of only one dominant attribute at a time, resulted in the significant positive correlation of three texture attributes to stickiness, enveloping, stringy, and tacky. These three terms make up the top tier of stickiness-contributing textures. It is noteworthy that the attributes cohesive and toothpacking, which belong to the cohesive and adhesive attribute categories hypothesized to correlate positively with stickiness, in fact correlate negatively with stickiness when assessed via TDS. When data from CATA testing, which allows unlimited attribute selection for each sample, is compared to TDS data, an increase in the number of sticky-contributing attributes is observed. In addition to the tier one attributes, which correlated positively to stickiness regardless of methodology, the attributes cohesive, deformable, and toothpacking also show significant or stronger positive correlations to stickiness. This result suggests that the terms cohesive, deformable, and toothpacking make up a second tier of stickiness-contributing terms that relate positively to stickiness when selected in addition to tier one terms (CATA), but relate negatively or negligibly to stickiness when selected instead of tier one terms (TDS). Only by combining insights from both TDS and CATA methodologies could this hierarchy of stickiness-contributing texture attributes be elucidated.

5.5 Discussion and conclusions

Comparisons of sensory evaluations across panelist type (i.e., trained or consumer), and sensory method (i.e., conventional descriptive analysis or alternative descriptive methods), have generated much interest and many recent publications (Gómez and others 1998; Hersleth and others 2005; Worch and others 2010; Ares and others 2015). This study probes the similarity between expert- and consumer-generated sensory data both through separate, panelist-tailored methods (TDS for trained panelists, CATA for consumers) and through an identical task (rating of stickiness intensity).

Analysis of attribute intensity ratings by consumers is not unprecedented (Reinbach and others 2014); however, the collection and use of consumer intensity ratings is generally ineffective due to the insufficient training of consumers given the difficulty of the task and resultant large variability in understanding of the attributes and use of the scale. In the identical rating task, we found that consumers and trained panelist showed strong agreement in their evaluation of the relative stickiness of samples within a product category, despite the complexity of stickiness as a textural perception. Trained panelists did utilize the upper end of the scale more readily than consumers, possibly due to greater familiarity with the sample set or greater confidence in their scale use. Overall, though scale use did differ among consumers and between the panels, the strong agreement between consumer and trained panelist evaluation of stickiness across a wide range of stickiness intensities should support the validity of trained panel stickiness evaluations in predicting consumer perceptions.

Similarly, the comparison of trained panelist- and consumer-generated texture profiles from panelist-tailored methods showed reasonable congruence. The significant differentiation between frequency of CATA term application by sample and the similarity in texture profile trends summarized by the CVA biplot generated from TDS data (Figure 2) and the PCA biplot generated from CATA data (Figure 3), suggest that consumers can, on average, apply even complex texture terms to samples in a discriminating way. This result supports previous research that has shown general agreement between sensory profiles generated by CATA data and data from conventional descriptive tests (Dooley and others 2010; Ares and others 2015).

Another contribution of this study involves the articulation and measurement of texture attributes that contribute to stickiness perception. The value of identifying contributing attributes of complex textures is highlighted in a frequently cited publication by Kokini and Cussler (1983), which shows that creaminess, a complex and difficult-to-measure texture attribute, can be predicted by scores for smoothness and thickness, both of which can be more reliably measured instrumentally. In this study, the characterization of the texture profile of caramel samples with varying degrees of stickiness gives insight into the texture properties that positively and negatively influence perception of stickiness in caramels.

Six terms were found to correlate positively to stickiness perception when assessed by TDS and/or CATA. These six terms were divided into two tiers, designating the strength of their positive contribution to stickiness perception based on the influence of attribute selection limitations on the magnitude and directionality of the correlation. Caramel samples that deform instead of break and present texture profiles dominated by the tier one stickiness-contributing

attributes enveloping, stringy, and tacky receive the highest stickiness ratings by both consumers and trained panelists. The strong correlations between the tier one attributes and stickiness agree with previous literature, including findings from Dunnewind and collaborators (2004), which found that 'long behavior' or 'necking' was highly predictive of sensory stickiness in custard desserts, and the commonly discussed interrelatedness of stickiness with surface adhesion, or "tacky" texture (Jowitt 1974; Kilcast and Roberts 1998; Adhikari and others 2001). The detailed, hierarchical profile of sticky texture in caramel materials illuminated by this study provides a framework for measuring and communicating facets of caramel sticky texture perception in future analyses.

This study provides a cumulative analysis of the influence of texture properties on overall stickiness perception. However, texture is the result of a dynamic process, and both the intensity of stickiness and the influence of contributing texture properties could change over time during mastication. For this reason, dynamic characterization of complex textures, such as stickiness, is recommended (Pascua and others 2013). Future studies should focus on analyzing the temporal influence of texture attributes on stickiness perception.

The interrelatedness of tactile and oral stickiness perception and the perception of stickiness-contributing texture properties was confirmed in this study. A strong positive correlation should be expected between tactile and oral stickiness, due to similarities in mechanisms of perceptions and compositional factors that affect tactile and oral texture (Foegeding and others 2015). However, direct comparisons between tactile and oral stickiness evaluations are scarce (Brennan and Mohamed 1984). Therefore, another possible extension of

this research is the characterization of the fundamental physical properties of the caramel materials that cause the concerted increase or decrease in the degree of tactile stickiness, oral stickiness, and related texture perceptions across the caramel sample set. Understanding of the cause of varying texture profiles from a physical or formulation-based perspective would enable versatile control of product texture.

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5.7 Figures and tables

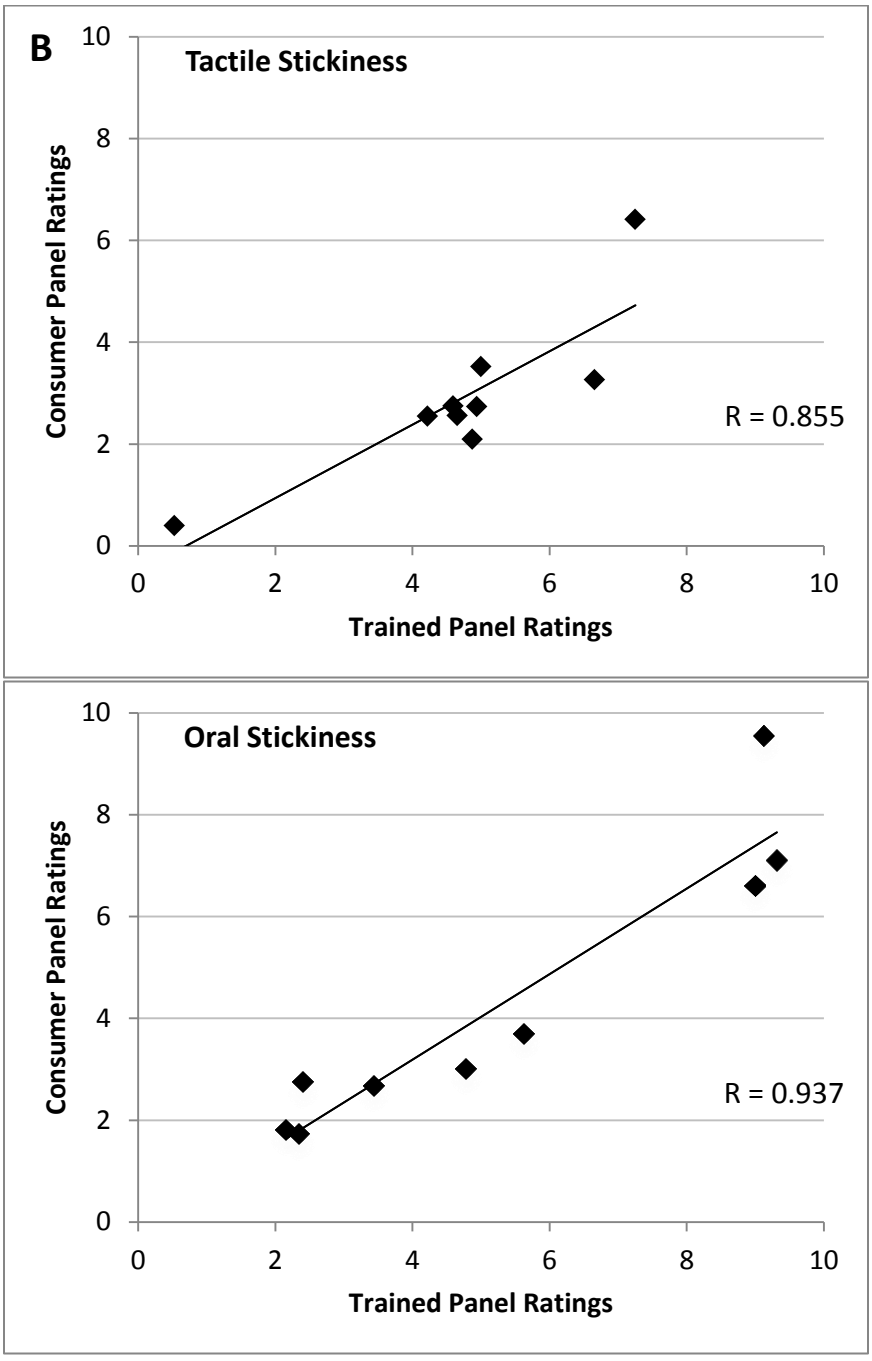

Figure 5.1. Mean stickiness ratings for caramel samples by consumer panelists plotted against mean stickiness ratings by trained panelists for tactile (A) and oral (B) evaluations of sample stickiness.

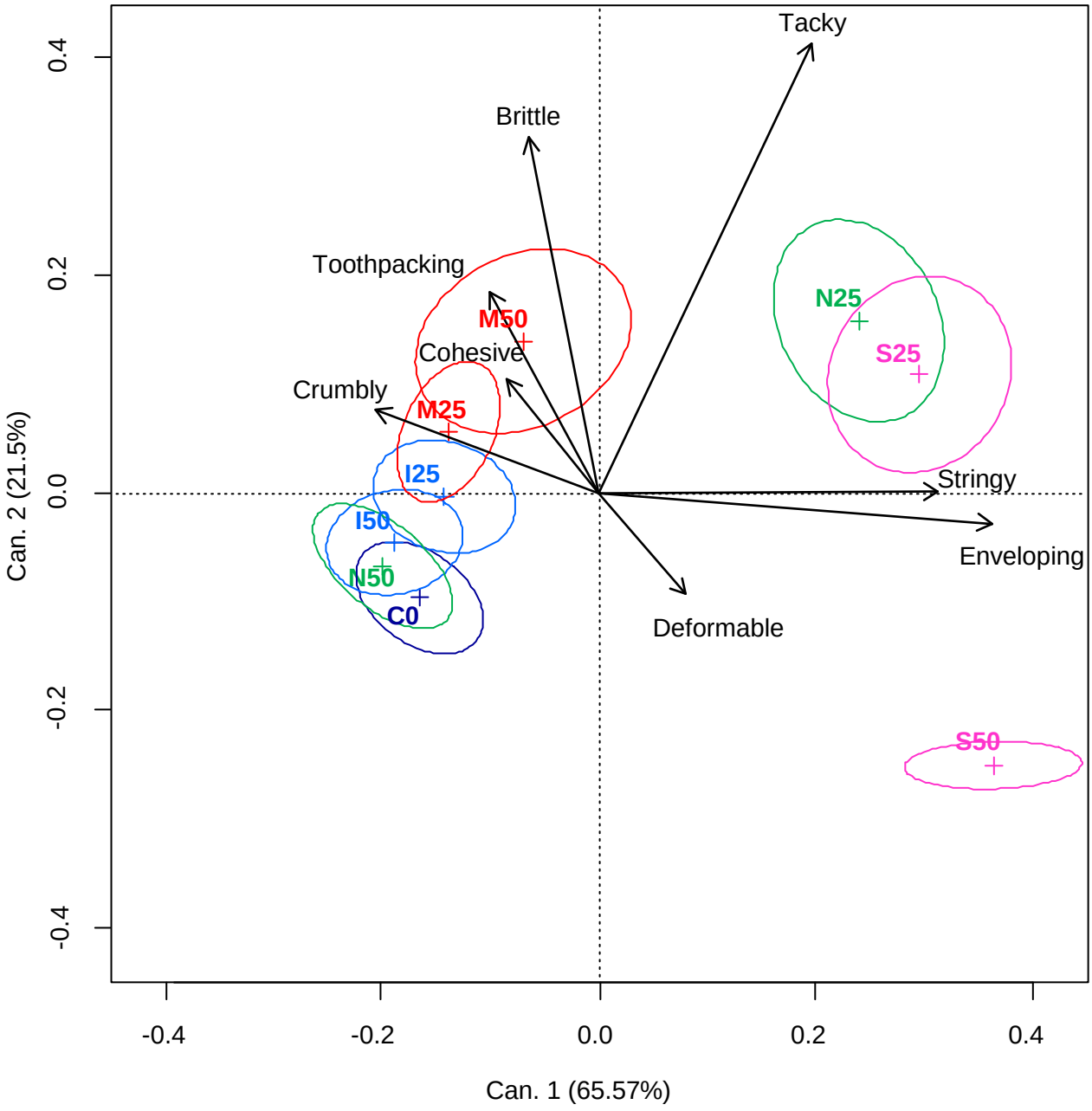

Figure 5.2. Hotelling canonical variates analysis (CVA) biplot of temporal dominance of sensation (TDS) duration data. Sample center positions are marked with a "+" and encircled by 90% confidences ellipses. Sample code names, center marks, and confidence ellipses are color-coded by the sugar alcohol utilized in the formula. Sample code names and color schemes are as follows: C0 stands for full-sugar control (navy blue); I stands for isomalt (blue); M stands for maltitol (red); N stands for mannitol (green); S stands for sorbitol (pink); 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol.

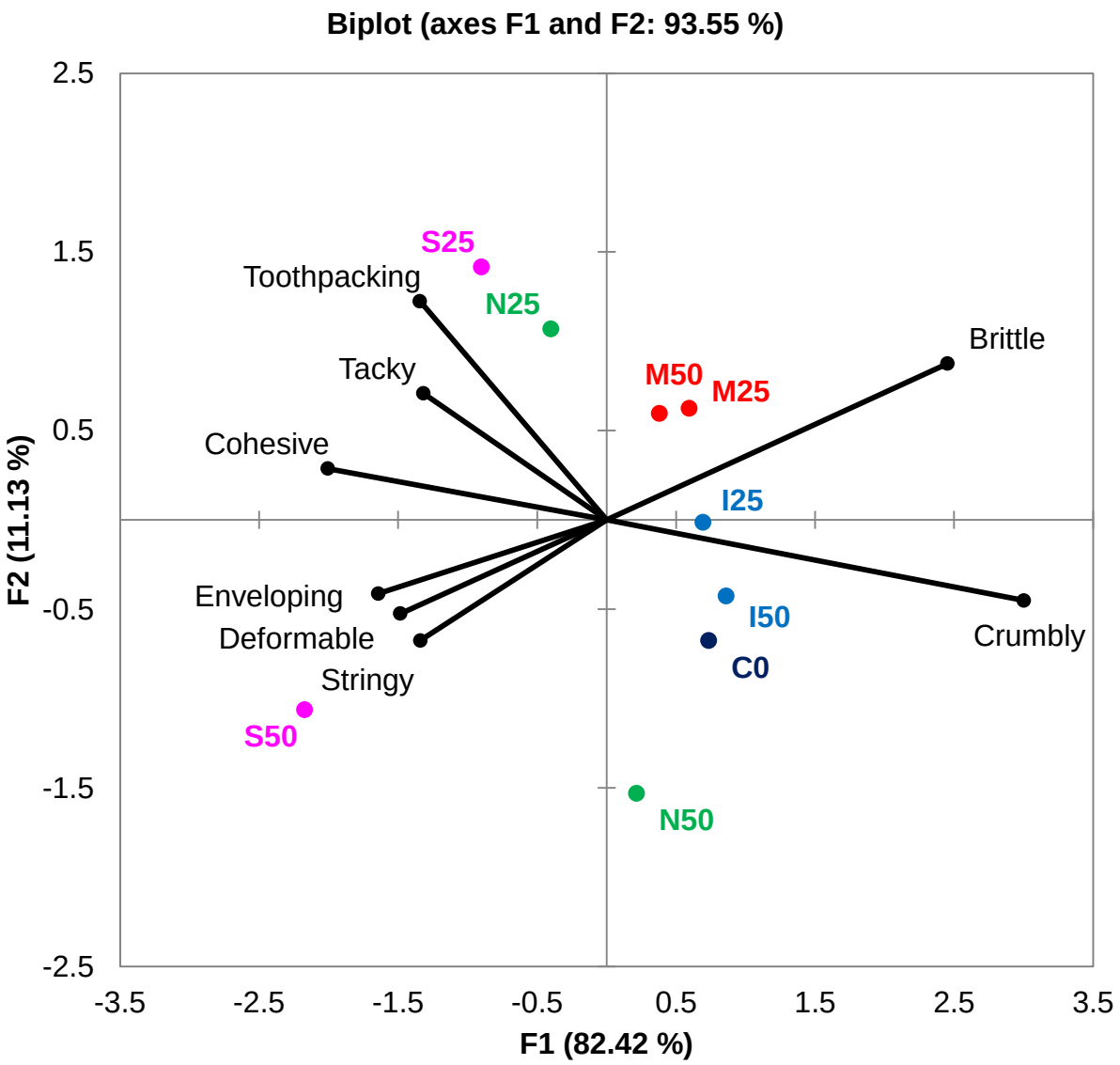

Figure 5.3. Covariance principal components analysis (Cov-PCA) biplot of check-all-that-apply (CATA) frequency of selection data. Sample code names and color schemes are as follows: C0 stands for full-sugar control (navy blue); I stands for isomalt (blue); M stands for maltitol (red); N stands for mannitol (green); S stands for sorbitol (pink); 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol.

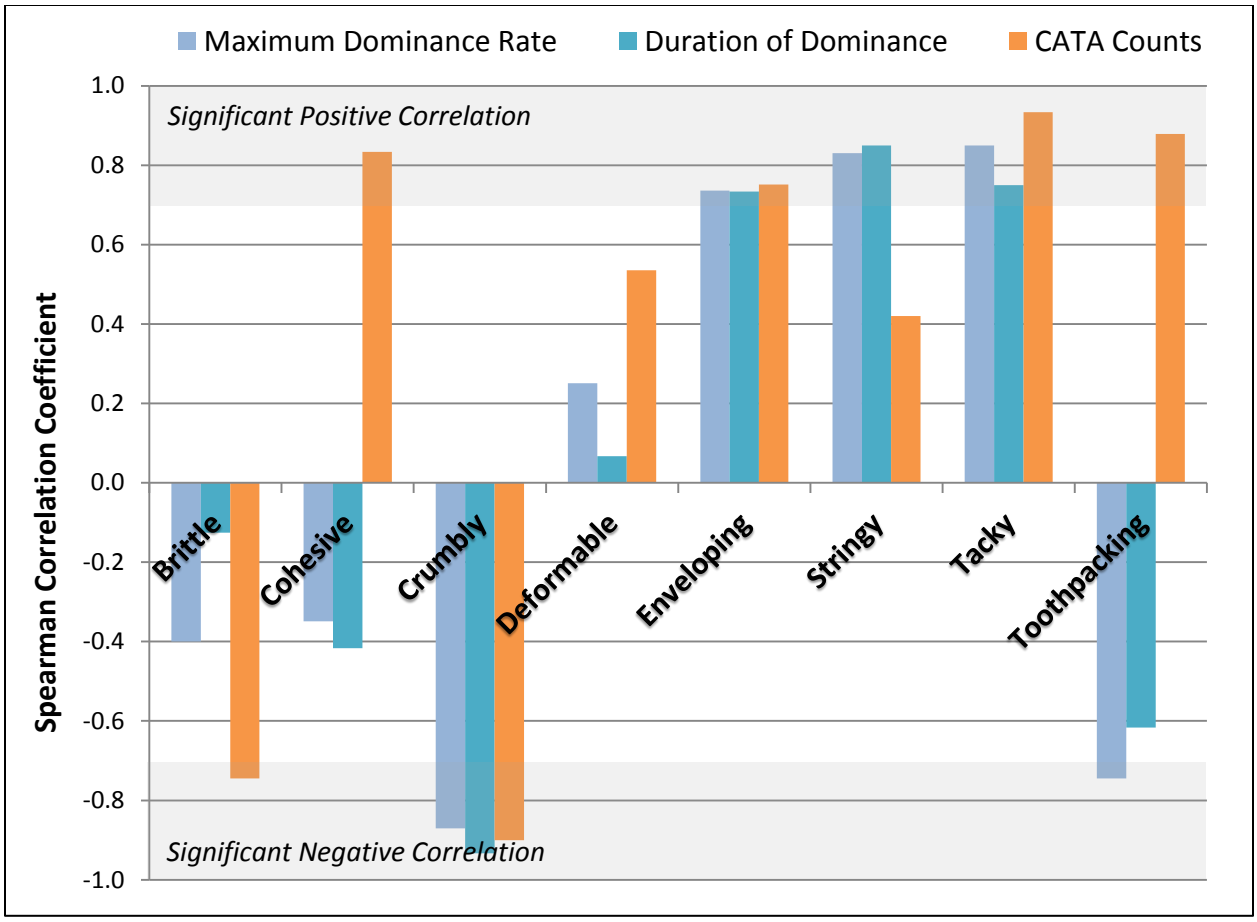

Figure 5.4. Spearman correlation coefficients relating temporal dominance of sensation parameters, maximum dominance rate and duration of dominance, to trained panelist oral stickiness ratings and check-all-that-apply (CATA) frequencies to consumer oral stickiness ratings. Bars extending into the shaded region at the extreme maximum and minimum ends of the y-axis indicate that the correlation coefficient represented is statistically significant at an α=0.05 significance level.

Table 5.1. Formulas for full-sugar control caramel samples and samples made with 25% or 50% sugar replacement by one of four sugar alcohols: isomalt, maltitol, mannitol, or sorbitol. Ingredient quantities are reported in grams.

Ingredient	**Sample formula with ingredients in grams**		
	Full-Sugar Control	**25% Sugar Replacement**	**50% Sugar Replacement**
Brown sugar	490	317.5	145
Corn syrup	400	400	400
Sugar alcohol	0	172.5	345
Corn oil	100	100	100
Salt	5	5	5
Baking soda	5	5	5
Formula Total	**1000**	**1000**	**1000**

Table 5.2. Texture attributes selected by the trained panel to be relevant to stickiness perception, researcher designated attribute categories, attribute references, and attribute definitions used in the caramel temporal dominance of sensation study. Attribute names were also used in the check-all-that-apply exercise as part of the consumer test.

Caramel Texture Terms and References			
Attribute	**Category**	**Reference Product; Manufacturer**	**Definition**
Brittle	Bend vs. Break	Life Savers hard candies; Wm. Wrigley Jr. Company	Sample shows singular breakage after force is applied
Cohesive	Cohesive	Jolly Rancher Chews; The Hershey Company	Pieces reform together
Crumbly	Bend vs. Break	Peanut Butter Bars; Atkinson Candy Co.	Sample shows continuous breakage after force is applied
Deformable	Bend vs. Break	Charleston Chew Bars; Tootsie Roll Industries	Easy to change shape without breaking when force is applied
Enveloping	Adhesive	Sugar Babies; Tootsie Roll Industries	Leaves residual material on side surfaces of teeth
Stringy	Adhesive/ Cohesive	Sugar Babies; Tootsie Roll Industries	Forms strings as you pull teeth apart
Tacky	Adhesive	Turkish Taffy; Bonomo Turkish Taffy, LLC	Adheres to teeth, resists separation
Toothpacking	Adhesive	Werther's Original Caramel Hard Candies; Storck USA, L.P.	Packs in teeth - related to quantity that packs

Table 5.3. Average tactile and oral stickiness ratings for caramel samples evaluated by consumer and trained panelists with Analysis of variance (ANOVA) and Least Significant Difference (LSD) means separation. Mean stickiness ratings of samples in each column with the same letter superscript are not significantly different. The LSD value was calculated based on an α value of 0.05 and is given at the bottom of the table for each column.

	Consumer Data		Trained Panelist Data	
Sample*	Tactile Stickiness	Oral Stickiness	Tactile Stickiness	Oral Stickiness
C0	2.09^{D}	1.73^{E}	4.88^{BC}	2.34^{E}
I25	2.56^{C}	2.68^{D}	4.66^{BC}	3.44^{D}
I50	2.55^{C}	1.81^{E}	4.22^{C}	2.16^{E}
M25	2.73^{C}	3.01^{D}	4.94^{BC}	4.78^{C}
M50	2.75^{C}	3.71^{C}	4.59^{BC}	5.63^{B}
N25	3.52^{B}	6.60^{B}	5.00^{B}	9.00^{A}
N50	0.40^{E}	2.75^{D}	0.53^{D}	2.41^{E}
S25	3.27^{B}	7.11^{B}	6.66^{A}	9.31^{A}
S50	6.41^{A}	9.55^{A}	7.25^{A}	9.13^{A}
Sample F-value	98.08	195.89	45.69	134.22
LSD	0.44	0.55	0.77	0.52

*C0 stands for full-sugar control; I stands for isomalt; M stands for maltitol; N stands for mannitol; S stands for sorbitol; 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol

Table 5.4. Results of hierarchical clustering analysis of centered consumer stickiness ratings of caramel samples, including cluster size (n) and F-values by cluster (F) produced by the varclus procedure for one through three clusters.

Number of clusters	Clusters	n	F
1	**P1C1**	75	143
2	**P2C1**	34	96.5
	P2C2	41	79.9
3	**P3C1**	30	84.5
	P3C2	37	121
	P3C3	8	5.29

Table 5.5. Pearson correlation coefficients relating consumer and trained panelist tactile and oral stickiness ratings. Correlation coefficients in bold are significantly different from 0 at an α=0.05 significance level.

Variables	Consumer Tactile	Consumer Oral	Trained Tactile	Trained Oral
Consumer Tactile	**1**			
Consumer Oral	**0.820**	**1**		
Trained Tactile	**0.855**	0.645	**1**	
Trained Oral	**0.736**	**0.937**	**0.689**	**1**

Table 5.6. Results of Cochran's Q testing on check-all-that-apply (CATA) data, including p-values comparing attribute use between samples and decimal values indicating the proportion of panelists who applied each attribute to each sample. Proportion of attribute selection values in each row with the same superscript letter did not differ significantly between the given samples at a significance level of α=0.05.

Attributes	p-values	C0	I25	I50	M25	M50	N25	N50	S25	S50
Brittle	< 0.0001	0.854^{d}	0.817^{d}	0.817^{d}	0.829^{d}	0.744^{cd}	0.634^{bcd}	0.476^{b}	0.537^{bc}	0.037^{a}
Cohesive	< 0.0001	0.244^{ab}	0.171^{a}	0.146^{a}	0.207^{a}	0.256^{ab}	0.439^{bc}	0.268^{ab}	0.622^{cd}	0.720^{d}
Crumbly	< 0.0001	0.793^{c}	0.805^{c}	0.829^{c}	0.732^{c}	0.695^{c}	0.402^{b}	0.634^{bc}	0.146^{a}	0^{a}
Deformable	< 0.0001	0.268^{a}	0.220^{a}	0.183^{a}	0.195^{a}	0.159^{a}	0.366^{a}	0.341^{a}	0.341^{a}	0.683^{b}
Enveloping	< 0.0001	0.122^{a}	0.098^{a}	0.049^{a}	0.098^{a}	0.122^{a}	0.134^{a}	0.049^{a}	0.183^{a}	0.646^{b}
Stringy	< 0.0001	0.110^{a}	0.098^{a}	0.098^{a}	0.012^{a}	0.073^{a}	0.134^{a}	0.146^{a}	0.134^{a}	0.549^{b}
Tacky	< 0.0001	0.134^{a}	0.207^{ab}	0.159^{a}	0.280^{abc}	0.415^{bcd}	0.561^{d}	0.293^{abc}	0.500^{cd}	0.524^{d}
Toothpacking	< 0.0001	0.366^{ab}	0.549^{bcd}	0.427^{abc}	0.610^{cde}	0.585^{bcde}	0.707^{de}	0.232^{a}	0.793^{e}	0.793^{e}

C0 stands for full-sugar control; I stands for isomalt; M stands for maltitol; N stands for mannitol; S stands for sorbitol; 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol

Chapter 6: Temporal texture profile and identification of glass transition temperature as an instrumental predictor of stickiness in a caramel system

6.1 Abstract

Stickiness is an important texture attribute in many food systems, but its meaning can vary by person, product, and throughout mastication. This variability and complexity makes it difficult to devise analytical tests that accurately and consistently predict sensory stickiness. Glass transition temperature (T_g) is a promising candidate for texture prediction. Our objective is to elucidate the temporal profile of stickiness in order to probe the relationship between T_g and dynamic stickiness perception. Nine caramel samples with diverse texture and thermal profiles were produced for sensory testing and differential scanning calorimetry. Sixteen trained panelists generated stickiness-relevant terms to be used in a subsequent temporal dominance of sensation (TDS) test with the same panelists. Following the TDS study, these panelists also rated samples for overall tactile and oral stickiness. Stickiness ratings were then correlated to TDS dominance parameters across the full evaluation period and within the first, middle, and final thirds of the evaluation period. Samples with temporal texture profiles dominated by tacky, stringy, and enveloping attributes consistently received the highest stickiness scores, although the correlation strength varied by time period. T_g was found to correlate well with trained panelist and consumer ratings of oral ($R^2_{trained}$=0.85; $R^2_{consumer}$=0.96) and tactile ($R^2_{trained}$=0.78; $R^2_{consumer}$=0.79) stickiness intensity, and stickiness intensity ratings decreased with T_g of completely amorphous samples. Further, glassy samples followed a different texture trajectory (brittle-cohesive-toothpacking) than rubbery samples (deformable-

tacky-enveloping). These results illuminate the dynamic perception of stickiness and support the potential of T_g to predict both stickiness intensity and texture trajectory in caramel systems.

6.2 Introduction

The critical role of texture in influencing consumer acceptance of foods and satiety from foods has been established in the literature; however, the complexity and dynamic nature of food texture perception continues to challenge both sensory and instrumental texture measurements (Jowitt 1974; de Graaf and Kok 2010; Van Vliet 2010; Pascua and others 2013). The difficulty in understanding and measuring texture stems from the sheer quantity and variety of sensory inputs that combine to cause a given texture perception, as well as the continuous changes in sample properties and perceived texture as the sample is prepared into a bolus for swallowing during mastication (Szczesniak 1963a; Hutchings and Lillford 1988; Szczesniak 2002; Foegeding and others 2015). More simply put, texture is not an intrinsic property of foods, but rather its perception results from active motor and sensory interaction with foods during handling and mastication (Jowitt 1974).

Measurement of stickiness is particularly hindered because sticky texture encompasses many of the aforementioned sources of complexity (Kilcast and Roberts 1998; Adhikari and others 2001). With relevance to a wide array of product categories, including confectionary, dairy, and powdered products, stickiness also holds different meanings depending on the food context in which it is perceived (Kilcast and Roberts 1998; Adhikari and others 2001). The degree to which a food sticks to packaging materials, fingers, and oral surfaces can all influence consumer perception of the overall stickiness of a product (Kilcast and Roberts 1998). It may be

due to the diversity of sticky products and the impact of product context on understanding of stickiness that no consensus exists regarding which forces and factors contribute to stickiness, though adhesiveness, cohesiveness, viscosity, viscoelasticity have all been proposed as key factors (Adhikari and others 2001).

How then can texture, and stickiness specifically, of food materials be measured? Many studies have measured stickiness or adhesiveness in products using sensory, instrumental, and combinatory techniques (Lee and Resurreccion 2001; Adhikari and others 2003; Steiner and others 2003; Dunnewind and others 2004; Goode and others 2013; Wagoner and others 2016). As Szczesniak emphasized, texture is a sensory property (Szczesniak 2002). Therefore, sensory methods often provide the most complete and useful understanding of the texture properties of foods. Temporal methods, including time-intensity (TI), temporal dominance of sensation (TDS), and temporal check-all-that-apply (T-CATA), have contributed an additional dimensional to conventional descriptive profiling methods by allowing researchers to create a dynamic texture profile, sometimes termed the texture or sensory trajectory, which encompasses the changes in texture properties and the intensity of those properties over time during mastication (Lee and Pangborn 1986; Pineau and others 2003; Lancaster and Foley 2007; Labbe and others 2009; Lenfant and others 2009; Castura and others 2016).

Instrumental methods have long been sought as time- and cost-effective means of texture measurement (Szczesniak 1963b; Chen and Opara 2013). Additionally, instrumental characterization of fundamental food properties can illuminate structural and compositional underpinnings of perceived texture properties, enabling more informed testing and

modification of food texture. Rheometers and texture analyzers are frequently utilized to predict or explain sensory texture properties (Breene 1975; Bourne 1978; Chung and others 1999; Lee and Resurreccion 2001; Bourne 2002; Steiner and others 2003; Gupta and others 2007; Brighenti and others 2008; Barra and Mitchell 2013; Wagoner and others 2016). Moisture content also plays a role in food texture, particularly in confectionary systems, and has been correlated to texture properties, including stickiness (Pereira and others 2002; Mendenhall and Hartel 2014). These metrics have shown product- and attribute-specific success in predicting or explaining texture perceptions, but each has limitations, especially in predicting texture attributes, such as stickiness, which are influenced by multiple food properties and oral processing parameters (Hutchings and Lillford 1988; Chen and Opara 2013).

Despite the variety of forces and factors that contribute to stickiness, the authors are unaware of a previous attempt to explore and measure sub-attributes of stickiness perception, as has been done for another complex texture attribute, creaminess (Kokini and Cussler 1983; Weenen and others 2005). Caramel materials offer a valuable and relevant model system for texture and stickiness research due to the importance of stickiness to the texture profile of caramel products and the difficulty in measuring stickiness within caramel systems (Mendenhall and Hartel 2014). The term “caramel” can have both broad and specific meanings; in this case, the term is used to describe a lipid- and carbohydrate-based confectionary model system which has undergone caramelization. The first objective of this study is to quantify the temporal contribution of stickiness-relevant texture attributes to overall stickiness perception in a caramel system. We hypothesized that stickiness would be positively influenced by cohesive and adhesive properties of the material in a time-dependent fashion.

The emergence of the food materials science approach has showcased the potential of thermal properties, and particularly of T_g, as instrumental predictors of food texture (Slade and others 1991; Martinez and Chiralt 1995; Huang and Hsieh 2005; Payne and Labuza 2005). The texture of caramel materials, which is largely controlled by the properties of the amorphous, carbohydrate-based continuous phase of the caramel, is well suited to correlations with this instrumental approach (Heim 2003; Mendenhall and Hartel 2014). Therefore, the second objective of this study is to relate sample T_g to oral and tactile texture properties in a caramel system. We hypothesized that decreasing T_g will correspond to increasing oral and tactile stickiness and corresponding changes to texture profile.

6.3 Materials and methods

Caramel preparation

Three caramel coating formulas designed to match the properties of caramel coatings used in commercial caramel popcorn products were previously developed (Mayhew and others 2016). The large-scale dark (LD) formula, which was named for both the signature dark color and flavor profile and the high volume of production, was used exclusively in this study. Commercial products represented by the LD formula were characterized as having a sweet and molasses-like flavor profile. In the LD control formulation, the ingredient composition is as follows: 49% brown sugar, 40% corn syrup, 10% corn oil, 0.5% salt, and 0.5% baking soda. Caramel sample sets with diverse texture profiles were created through replacement of 25% or 50% of sugar in the formula with one of four sugar alcohols: isomalt, maltitol, mannitol, or sorbitol. Samples were produced in 1000g batches and were coded as follows: C0 for control with 0% sugar replacement, I for isomalt, M for maltitol, N for mannitol, S for sorbitol, 25 for

25% sugar replacement, and 50 for 50% sugar replacement. Ingredients were stirred and heated in a stainless steel pan on a gas range until the mixture reached 150°C, within the range of temperatures corresponding to the "hard crack" stage of sugar cooking. The temperature of the mixture was monitored continuously with a high accuracy Traceable® thermocouple (Thermo Fisher Scientific Company, Waltham, Massachusetts, U.S.A.). The mixture was then transferred to silicon molds (WOOTOP, Shenzhen, Guangdon, China) to form 1.0 cm^3 cubes, allowed to cool and solidify at 22°C, vacuum sealed, and stored in a lidded, opaque tub prior to sensory and analytical testing.

Sensory tests

Temporal dominance of sensation (TDS) testing was conducted to assess the dominance of texture attributes over time during mastication. Of 41 panelists who were screened by oral health and ability to discriminate between samples and generate meaningful texture descriptors, 16 (11 female, 5 male, ages 22-45 yrs.) panelists were accepted and signed up to participate in the study. These 16 panelists were trained in descriptive and TDS methods prior to testing and developed a lexicon of texture terms with relevance to sticky texture, including the terms brittle, cohesive, crumbly, deformable, enveloping, stringy, tacky, and toothpacking, for use in the TDS test. Method training and terms generation took place over eight, one-hour sessions. A rinse protocol consisting of a warm water rinse, followed by a bite of carrot, followed by a room temperature water rinse was used consistently by panelists between sample evaluations. Additionally, panelists were instructed to expectorate both samples and rinses.

Throughout training and testing, sample cubes were presented in lidded 29.5mL cups labeled (Solo Cup Company, Inc., Chicago, IL) with random 3-digit codes. Following training and booth practice, panelists participated in TDS testing of samples in sensory booths (booths maintained at 22°C and 33% relative humidity) using TimeSens® software (www.timesens.com). A William's Latin square randomization design was applied to assign unique sample evaluation orders for each panelist, and panelists evaluated each of the 9 distinct samples in triplicate.

Stickiness intensity evaluation was conducted by trained panelists and consumers for both tactile and oral stickiness of the sample set. Sample cubes were consistently coded with random 3-digit codes and served in lidded 29.5mL cups (Solo Cup Company, Inc., Chicago, IL). The ballots for this portion of the sensory testing were constructed and administered using Qualtrics (Qualtrics, Provo, UT, U.S.A.). Seventy-five consumers with good oral health and who regularly consumed caramel products passed a screener and participated in two sensory test sessions. In the first session, consumers participated in hedonic evaluation of the samples and a CATA exercise using the same texture terms generated for the TDS study. This session doubled as a warm-up, allowing consumers to interact with the complete sample set prior to the more challenging tasks, which were presented in session 2. In the second session, the consumers evaluated the overall intensity of sample stickiness both by hand (tactile stickiness) and by mouth (oral stickiness). Thorough written instructions were provided to the consumer panelists, as well as a verbal overview of the procedure and any requested clarifications, but no formal training was administered.

The 16 trained panelists who participated in the TDS test also evaluated the overall tactile and oral stickiness intensity following all TDS data collection. In between tactile stickiness evaluations, panelists were instructed to clean fingers with a moist sponge and dry fingers with a napkin. In between oral stickiness evaluations, panelists were instructed to rinse their mouths with warm water, a bite of carrot, and room temperature water, expectorating all rinses and remnants of the sample. Each of 9 distinct samples was evaluated in a randomized order once by consumer and in duplicate by trained panelists.

Instrumental measurements

Water activity (a_w) was measured in triplicate to calculate average a_w values for all caramel samples. Samples were crushed or stretched to form a thin layer covering the bottom of sample cups. Measurements were made with an AquaLab 4TE instrument (Decagon Devices, Inc., Pullman, WA, U.S.A.) at 25.7 ± 0.7°C.

Moisture content was measured by vacuum oven drying of caramel samples (5.6 ± 1.2 g). Depending on their initial state, samples were either ground or stretched and spread into a thin layer in dry aluminum pans. Sample pans were randomized, placed in trays, and dried in a vacuum oven for 24 h at 60°C. Measurements were made in triplicate for each sample and percent moisture content (% wet basis, % wb) was calculated as the percent of initial sample weight lost during drying.

Differential scanning calorimetry (DSC) was utilized to characterize the thermal properties of caramel samples and sugar alcohol ingredients. The DSC was calibrated with an indium reference (known melting temperature of 156.6°C; known enthalpy of 28.71 J/g) to

ensure accuracy in temperature and enthalpy measurements. Caramel samples (7.5 $\pm$ 2.1 mg) and sugar alcohol ingredients (9.1 $\pm$ 1.0 mg) were massed and sealed in Tzero pans with hermetic lids (TA Instruments, New Castle, DE, U.S.A.) and loaded into a DSC Q2000 instrument with an autosampler (TA Instruments, New Castle, DE, U.S.A.) and refrigerated cooling system (RCS 90). At the start of each run, caramel samples were equilibrated at -40°C, and then heated to 200°C at a rate of 10°C/min.

Crystalline sugar alcohol samples were heated at a rate of 10°C/min until just melted; for isomalt, maltitol, mannitol, and sorbitol, the minimum final temperature to which the samples needed to be heated to achieve complete melting was 160°C, 155°C, 180°C, and 105°C, respectively. After the samples had been melted, they were rapidly cooled to -50°C to form an amorphous glass. Samples were then scanned at a rate to 10°C/min to 20°C higher than the temperature to which they had previously been heated, or to 180°C, 175°C, 200°C, and 125°C for isomalt, maltitol, mannitol, and sorbitol, respectively, to confirm the absence of an endothermic melting peak. Calibration and test runs were performed under dry nitrogen with a flowrate of 50 mL/min. Each caramel was tested in triplicate, and DSC scans were analyzed with Universal Analysis software (Version 4.4A, TA Instruments New Castle, DE, U.S.A.). Glass transition (T_g) parameters were analyzed with the Glass/Step Change function with Manual Tangent Selection to increase the accuracy of the measured transition height in samples displaying enthalpic relaxation in the glass transition region.

Statistical analysis

Extraction of TDS parameters, following time standardization, was accomplished using TimeSens® software (www.timesens.com). The two parameters of interest, duration of dominance and the maximum percent dominance rate, were selected and extracted for each attribute and sample both across the complete mastication period and within three time-frames (first, second, and final third of standardized total mastication and evaluation time).

Spearman correlation analysis in XLSTAT (Addinsoft, New York, NY, U.S.A.) was utilized to quantify the contribution of texture attributes to stickiness intensity across the mastication period. Correlations were deemed significant when $p \leq 0.05$. Stickiness intensity ratings were correlated to TDS parameters summed across mastication and within 3 time-frames to assess the temporal texture influence on stickiness intensity judgments.

Analysis of variance (ANOVA) and LSD means separation was used to compare caramel sample mean values of a_w, moisture content, T_g onset, T_g midpoint, T_g endpoint, and the change in specific heat at the T_g (Δc_p). All analysis was conducted with SAS statistical software (Version 9.4, SAS, Cary, NC, U.S.A.), and an alpha of 0.05 was used for all significance judgments.

Trajectory principal component analysis (PCA) was conducted to visualize the texture trajectory of caramel samples during the mastication period using TimeSens® software (www.timesens.com). The TDS data was time-standardized prior to trajectory PCA analysis; five time points were plotted for each sample and a smoothed trajectory curve was applied.

TDS bandplots were constructed using time-standardized TDS data in the TimeSens® software package (www.timesens.com). Only significantly dominant texture attributes (α=0.1) were included in the bandplots for each sample.

6.4 Results and discussion

Temporal correlation of texture terms to stickiness intensity

Figure 6.1 shows a strong positive correlation between stickiness and the dominance of enveloping, stringy, and tacky, termed tier one stickiness-contributing attributes. The correlation of stickiness with TDS parameters Maximum Dominance Rate (TDS-Max) and Duration of Dominance (TDS-Dur) from three time periods of evaluation shows that the coefficient of correlation changes across mastication for all texture attributes analyzed (Figure 6.1). The TDS-Max of both enveloping and stringy is significantly positively correlated to stickiness in all three periods of mastication, although the correlation coefficients for enveloping and stringy peak in the first and second periods, respectively. The correlation of the TDS-Max of tacky is only significantly correlated to stickiness in the first and second period and peaks in the first period of mastication. TDS-Dur parameters for the tier one terms show a similar relationship to stickiness. Subtle differences include a loss of significant correlation of enveloping during the second period, a lower initial correlation and higher peak correlation in the second period for stringy, and an earlier decline in the correlation coefficient of tacky. Stronger correlation coefficients when the TDS-Max parameter is selected signifies a greater degree of simultaneous panelist agreement about the most dominant attribute, while stronger correlation coefficients for the TDS-Dur parameter speak to a more enduring dominance of the given attribute within the mastication period of interest.

The attributes cohesive and deformable exhibit a change in the direction of correlation with a change in mastication period: TDS-Max and TDS-Dur parameters of both correlate positively to stickiness in the first period and negatively in the second and third periods. TDS-Max and TDS-Dur parameters of crumbly show significant negative correlations to stickiness in all periods of mastication, with the most strongly negative correlation occurring in the second period. Toothpacking TDS-Max shows a significant negative correlation to stickiness in the second and third period, while the negative correlation of TDS-Dur to stickiness is statistically significant only in the third period. It is important to note that a negative correlation to stickiness does not imply that the attribute precludes stickiness perception. Even given the wide range of stickiness ratings observed in this sample set, each caramel sample elicits some degree of stickiness perception. Texture attributes with negative correlations to stickiness therefore signify a lower relative stickiness in the samples dominated by those textures, rather than an absence of stickiness.

The time-dependence of correlations between texture attributes and stickiness intensity ratings can be explained by differences in perceived stickiness elicited by different progressions of dominant texture properties. Attributes deformable and cohesive may be dominant initial, but not final, components of a highly sticky texture progression, leading to a shift from positive to negative correlations to stickiness after the first mastication period. Similarly, toothpacking may negatively correlate significantly to stickiness in the final periods of mastication not because toothpacking detracts from stickiness, but because a texture progression with an ending dominated by toothpacking is less sticky than a progression ending with dominant stringy and enveloping sensations. Therefore, a highly sticky texture progression may be

composed of attributes cohesive and deformable in the first period and tier one attributes, enveloping, stringy, and tacky, in any period, while a sample producing a texture progression dominated initially by crumbly and ending in toothpacking would receive a much lower overall stickiness rating.

Instrumental characterization

Caramel samples exhibited statistically significant, but relatively small differences in average moisture content and a_w values (Table 6.1). The average moisture content of samples ranged from 3.22 to 4.31 % wet basis, and the average a_w of samples ranged from 0.245 to 0.352. Trends in sample a_w did not correspond to trends in moisture content. For example, the sample with the highest moisture content, N25, and lowest moisture content, S25, had equal a_w.

Trends in thermal properties of caramel samples provided more meaningful separation of samples than moisture content or a_w. Pronounced differences in T_g were observed between samples, as T_g systematically decreased as a function of decreasing sugar alcohol T_g (Table 6.1). Minor differences in mean separation exist between T_g parameters, onset, midpoint, and endpoint temperatures, due to variation in the width of the glass transition between samples. However, general trends were conserved. The control sample, C0, had the highest T_g values, followed by samples I25 and I50, all of which are glassy at room temperature. The T_g of sample M25 begins near room temperature, the T_g range of sample M50 overlaps conventional room temperature ranges, suggesting that samples M25 and M50 are likely primarily glassy, but partially rubbery at room temperature. Samples N25, N50, S25, and S50 all completed the

transition from glassy to rubbery below 22 °C, indicating that these samples were in the rubbery state at room temperature. The T_g of S50 was exceptionally low, with an average T_g onset of -11.5 °C.

All samples were fully in an amorphous state except for N50, which contained both amorphous and crystalline material, as evidenced by the fact that only sample N50 displayed an endothermic peak corresponding to melting of crystalline material in its thermograms. Sample N50 also had a significantly lower step change in specific heat (Δc_p) at the glass transition than the remainder of the sample set, reinforcing the conclusion that sample N50 was not composed entirely of amorphous material. The unique thermal profile of N50 can be attributed to the strong tendency of mannitol to crystallize instead of forming a glass upon cooling, a tendency which was inhibited by the low concentration of mannitol in N25, but displayed when higher concentrations of mannitol were present in N50.

Correlation of T_g to sensory stickiness

In completely amorphous caramel samples, T_g midpoint shows a strong negative correlation to consumer and trained panelist evaluation of both tactile and oral stickiness (Figure 6.2). Although T_g onset and T_g endpoint showed similar correlations to stickiness ratings, T_g midpoint correlations with stickiness ratings were chosen for inclusion in this paper because T_g midpoint is the most commonly reported T_g parameter in the literature. The negative correlation between T_g and stickiness has intuitive meaning: the more rubbery, and less glassy, an amorphous sample is, the greater the intensity of perceived stickiness. Though the directionality of the correlation is intuitive, the high magnitude of correlation between an

instrumental metric, T_g, and sensory evaluation of stickiness exceeded expectations. In particular, the correlation between Tg midpoint and sensory oral stickiness ratings observed in this study was stronger than most previously reported correlations between sensory stickiness and instrumental metrics (Steiner and others 2003; Dunnewind and others 2004; Wagoner and others 2016).

Correlation coefficients relating T_g midpoint to average tactile stickiness scores by consumer evaluation and trained panelist evaluation are similar and lower in magnitude, 0.79 and 0.78, respectively, because the true relationship between tactile stickiness and T_g appears to be less linear than that of oral stickiness and T_g. Perceived tactile stickiness is relatively constant for sample with a T_g midpoint > 22 °C, then increases more rapidly as T_g midpoint decreases below 22 °C. Oral stickiness scores correlate more strongly to T_g due to the more linear relationship between the two metrics. Correlations of T_g midpoint with oral stickiness scores also differ more between panel types, as T_g correlates more strongly with consumer stickiness ratings (0.964) than with trained panelist stickiness ratings (0.853). This difference in correlation coefficients is likely caused by the greater spread in average stickiness scores for the three highest rated samples, N25, S25, and S50, by consumers (6.6, 7.1, and 9.6) compared to trained panelists (9.0, 9.31, and 9.13).

Differences in consumer and trained panelist scale use are also evident in the y-intercept of trendlines between data sets from the two panels. Trendline slopes are similar between consumer and trained panelist evaluations, but trained panelist evaluations are shifted higher on the y-axis, which represents average stickiness intensity rating, due to

conservative use by some consumers of the high end of the scale. The slope of the trendline relating stickiness ratings to T_g midpoint is more shallow for tactile stickiness than oral stickiness, due to the wider range of stickiness ratings applied to samples when evaluated by mouth. However, the consistency in trendline slopes indicates that consumers and trained panelists are aligned in their assessment of the relative stickiness of caramel samples.

Trajectory principal component analysis

Trajectory PCA of caramel samples reveals that the impact of sample T_g on texture profile extends beyond predictions of stickiness intensity (Figure 6.3). Two general categories of texture progressions can be seen in the trajectory PCA biplot. The first pathway begins with dominant brittle or crumbly texture, succeeded by dominant cohesive texture, and ending with dominant toothpacking. The alternative progression follows a general pathway from dominant deformable texture, through dominant tacky and stringy textures, and ends with dominant enveloping texture. Samples with T_g midpoint > 22 °C, i.e., samples that are glassy at room temperature, follow the first category of texture progression. Conversely, samples with T_g midpoint < 22 °C, i.e., samples that are rubbery at room temperature, follow the latter category of texture progression. The partially crystalline sample, N50, follows the first pathway due to the disruption of the continuous phase by crystalline mannitol, which results in a more crumbly texture. Given that initial state of the amorphous phase in purely amorphous materials dictates the general progression of dominant texture sensations in caramel samples, there is reason to believe that sample T_g can be used to predict temporal texture profile of amorphous food materials.

Dominant texture attributes over time

More detailed information about sample texture profile can be gleaned from the TDS bandplots (Figure 6.4) showing significantly dominant (α = 0.1) texture attributes for each sample across the time-standardized mastication period. The bandplots illustrate that each of the texture attributes is primarily associated with a certain period of time during mastication and/or with a certain subset of the sample set. For example, brittle is only ever significantly dominant in the initial stages of mastication, while enveloping is only significantly dominant in the middle and final stages of mastication. Texture attributes crumbly and stringy demonstrate the separation of attribute usage between subsets of the caramel samples, as crumbly and stringy are significantly dominant texture attributes in 8 of the 9 samples, but never significantly dominant in the same sample.

A more gradual trend in changing temporal texture profile is observed in the TDS bandplots when compared to the trajectory PCA trends. Although brittle is a dominant texture attribute in the early stages of mastication for all samples except for S50, other initially dominant textures shift from crumbly, to tacky, to deformable with decreasing sample T_g. All samples besides S50 exhibit dominant cohesive texture in the middle period of mastication; however, samples with high T_g also exhibit dominant toothpacking and crumbly texture, samples with intermediate T_g also exhibit dominant tacky and toothpacking texture, and samples with low Tg also exhibit dominant stringy and enveloping texture. The mastication period generally ends with dominant toothpacking texture, in the case of high T_g samples, or enveloping texture, in the case of most low T_g samples. The exceptions to this trend are C0, which has a high T_g but exhibits both dominant toothpacking and enveloping textures, and N50,

which has a low T_g but does not exhibit dominant enveloping texture, likely due to the presence of crystalline mannitol in the sample.

Summary of caramel properties by T_g

Based on the general categories of dominant texture trajectories observed in TDS bandplots, three categories were outlined based on T_g midpoint: $T_g > 30$ °C, 15 °C < T_g < 30 °C, and $T_g < 15$ °C. The boundaries between these categories may be explained by the relationship of the T_g of the material to the range of temperatures that the sample passes through during mastication, from room temperature (22°C) to approaching the oral temperature (37°C). The properties of caramel samples, including the intensity of perceived oral and tactile stickiness and texture trajectory, within each of these T_g midpoint ranges is summarized in Table 6.2. Caramel samples with high T_g, or samples which remain primarily in the amorphous glassy state throughout mastication, elicit low levels of both oral and tactile stickiness perception and follow a texture trajectory from brittle, through crumbly and cohesive, to toothpacking. Samples with an intermediate T_g, or samples that transition from glassy to rubbery during mastication as saliva is incorporated and samples approach the oral temperature, elicit low levels of tactile stickiness perception, but increased, or moderate, levels of oral stickiness perception. Samples in this category exhibit a texture trajectory that also begins with dominant brittle texture, but then leads into tacky and cohesive texture attributes in the middle period before ending with dominant toothpacking and enveloping textures. Finally, samples with low T_g, below 15 °C, elicit high intensity oral and tactile stickiness perception. These samples, which are in the rubbery amorphous state throughout the mastication process, are initially dominated

by deformable texture, followed by stringy texture, and ending in enveloping texture perception.

6.5 Conclusions

Replacement of sugar by sugar alcohols with decreasing T_g results in a corresponding decrease in system T_g. Temporal texture characterization and sensory stickiness measurement for this caramel sample set, which spans a wide range of system T_g values, illuminates promising correlations between system T_g and texture profile. The summary of sample texture properties for three T_g ranges given in Table 6.2 provides a simple means of predicting the stickiness and texture trajectory of confectionary materials instrumentally. Reducing unique sample texture profiles to three broad categories results in the loss of some specificity, but provides greater general applicability to developers of confectionary products.

One potential caveat of the texture prediction scheme proposed stems from the fact that the initial physical state, as characterized by distance between T_g and the initial temperature of evaluation, represents only the starting properties of the sample. This metric relates to tactile stickiness, in which material properties stay relatively constant throughout evaluation, in a straightforward fashion, but may relate more complexly to oral texture evaluation. Sample properties change across the mastication period as masticatory processes increase sample solvation and decrease sample particle size. This dynamic process of sample manipulation results in the dynamic perception of sample texture. Though measurement of sample T_g is decoupled from the changes in the sample caused by mastication, it nonetheless seems to provide meaningful correlations to perceived texture properties experienced by

panelists throughout the mastication process. The relevance of T_g to texture perception throughout mastication may be the result of the repeatable flow of texture attributes produced by the masticatory process. In other words, in addition to dictating the initially dominant texture properties, the initial physical state of the sample may lock the sample into a specific texture pathway. The extent to which initial physical state, or T_g, predicts temporal texture progression may be determined by the degree of similarity between the mastication process performed for the same samples by different individuals. The strength of average trends calculated from the texture perceptions of 16 individual panelists supports the general universality of temporal texture progression during mastication for a given sample and applicability of T_g to complete texture profile prediction.

Future research can focus on more precisely resolving the impact of food material T_g on perceived texture properties. Correlation coefficients relating T_g to both tactile and oral stickiness intensity were calculated based on the assumption of a linear relationship between the metrics, even though the fit of the linear trendline is less strong for tactile stickiness scores. The true relationship between T_g and tactile stickiness and cause of the change in trend near 22 °C merits further study.

This study establishes the relationship between system T_g and texture properties for a set of 9 caramel model systems. The expansion of the observed trends beyond the discrete sample set utilized in this study could also facilitate the application of this model to a broader range of confectionary materials, such as hard candies, toffees, and other primarily amorphous candies.

6.6 References

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6.7 Figures and tables

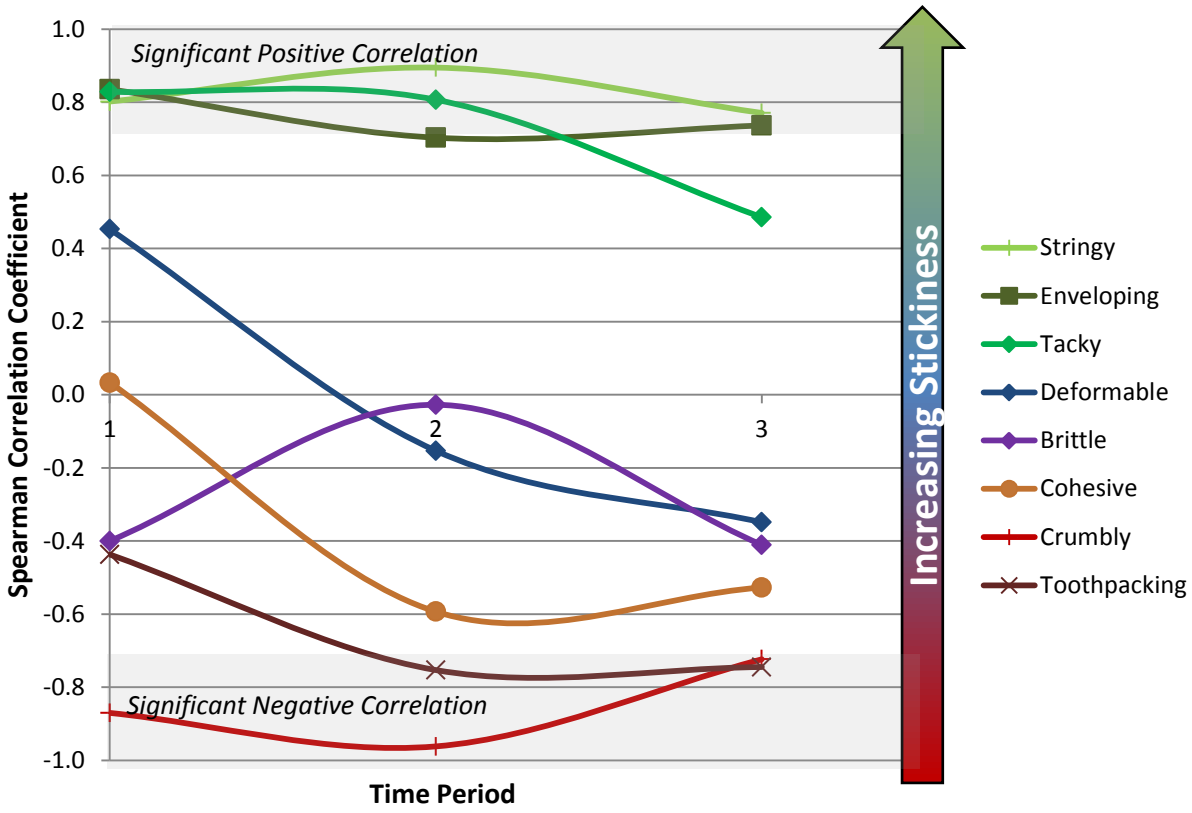

Figure 6.1. Spearman correlations of temporal dominance of sensation (TDS) maximum dominance rate (A) and TDS duration of dominance (B) parameters of texture attributes with trained panel mean oral stickiness ratings, calculated and plotted for the initial, middle, and final third of the time-standardized mastication period. Data points which fall in the shaded regions at the extreme maximum and minimum ends of the y-axis represent statistically significant correlation coefficients at an α=0.05 significance level.

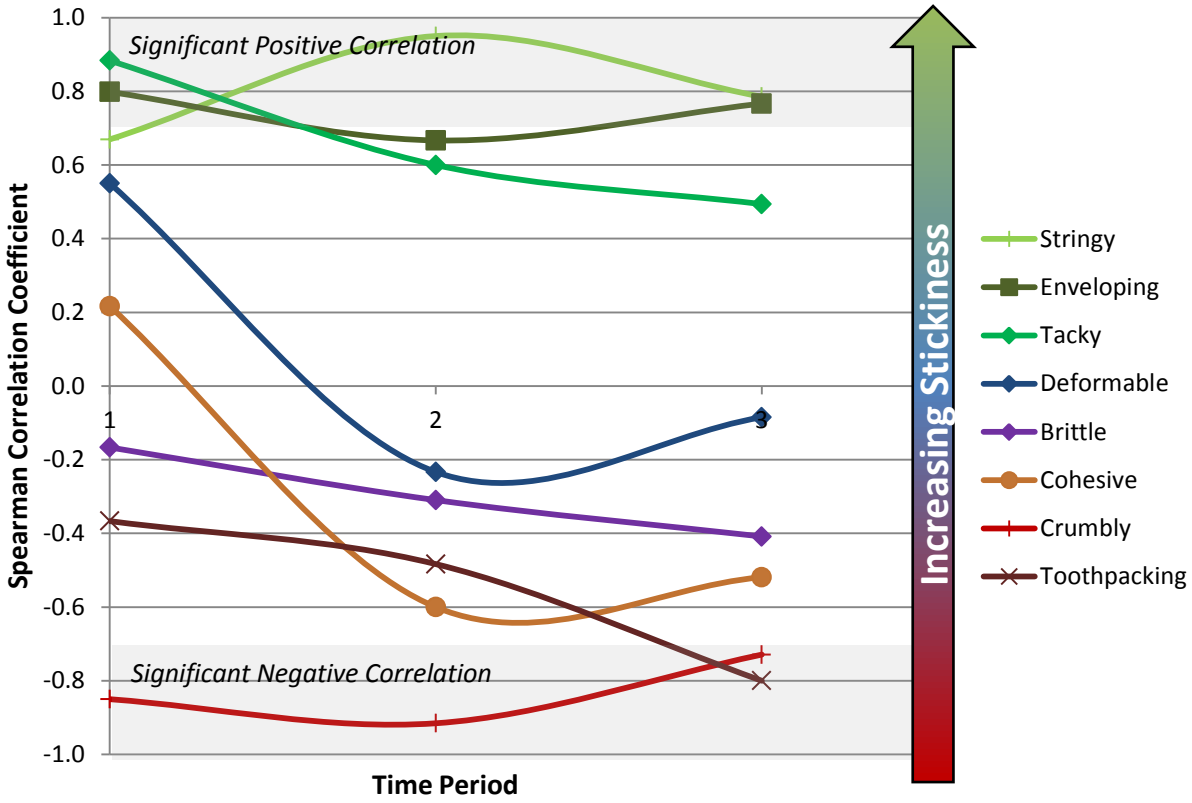

Figure 6.1 (cont.)

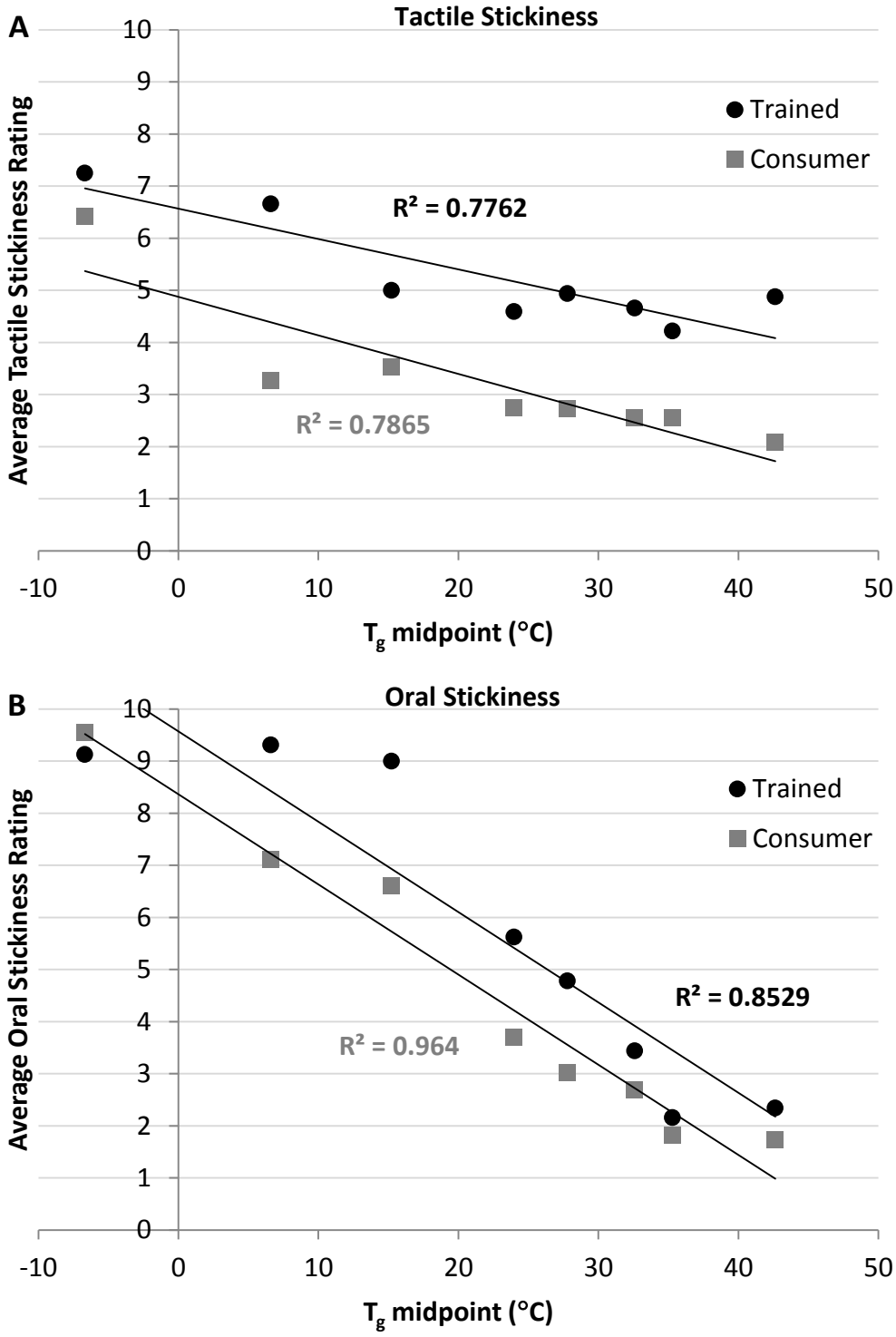

Figure 6.2. Average tactile (A) and oral (B) stickiness ratings by trained panelists and consumers of fully amorphous caramel samples plotted against sample average glass transition midpoint temperature (T_g midpoint).

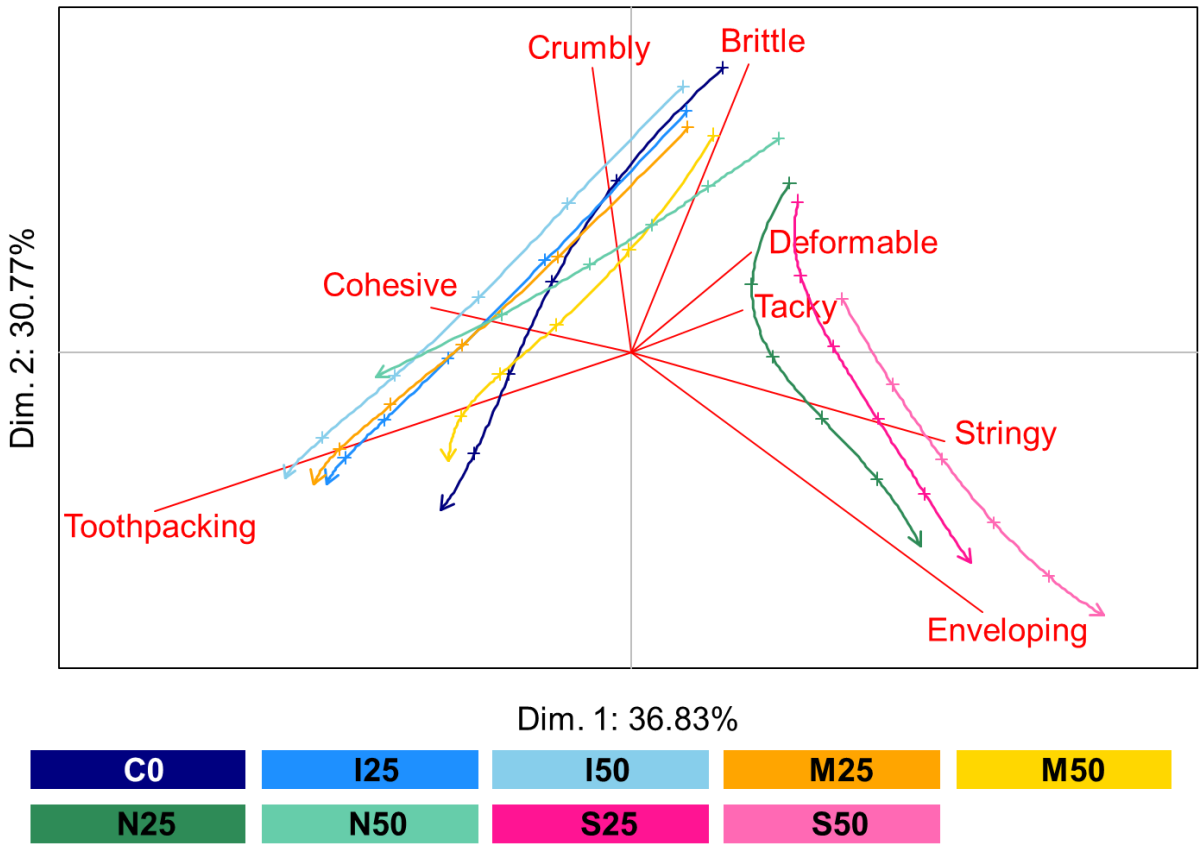

Figure 6.3. Trajectory principal component analysis (PCA) biplot with 5 points and moderate smoothing generated from temporal dominance of sensation (TDS) duration data. Samples are coded as follows: C0 stands for full-sugar control; I stands for isomalt; M stands for maltitol; N stands for mannitol; S stands for sorbitol; 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol.

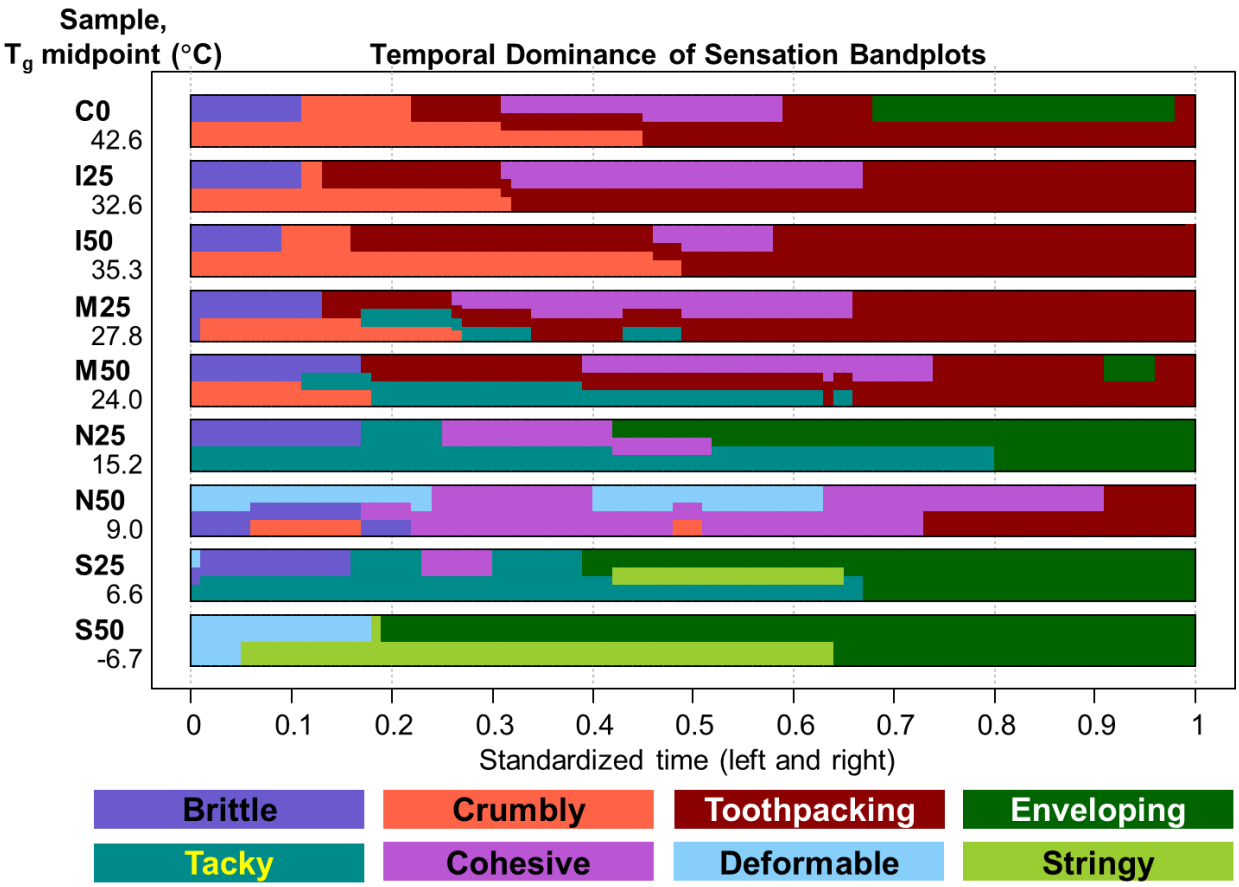

Figure 6.4. Temporal dominance of sensation (TDS) bandplots depicting significantly dominant texture attributes for each sample across the time-standardized mastication period, where the beginning of evaluation is represented by 0 and the end of evaluation by 1. Average T_g midpoint values are included for each sample for reference. Samples are coded as follows: C0 stands for full-sugar control; I stands for isomalt; M stands for maltitol; N stands for mannitol; S stands for sorbitol; 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol.

Table 6.1. Instrumentally measured properties of caramel samples, including moisture content reported as percent wet basis (% wb), water activity (a_w), and glass transition (T_g) onset, midpoint, and endpoint temperatures and the step change in the specific heat at the glass transition (Δc_p) of both caramel samples and sugar alcohol ingredients. Glass transition data for mannitol (N) come from the literature (Yu and others 1998). Measurements for caramel samples in each column with the same superscript are not significantly different (α=0.05).

Sample or Ingredient*	Moisture Content, % wb	a_w	T_g onset, °C	T_g midpoint, °C	T_g endpoint, °C	Δc_p, J/g°C
C0	3.22^{C}	0.285^{C}	39.1^{A}	42.6^{A}	46.0^{A}	0.93^{A}
I25	3.44^{BC}	0.334^{B}	27.3^{BC}	32.6^{BC}	37.9^{BC}	0.79^{A}
I50	3.45^{BC}	0.275^{E}	29.8^{B}	35.3^{B}	40.5^{AB}	0.95^{A}
M25	3.79^{B}	0.285^{C}	21.8^{CD}	27.8^{CD}	33.5^{CD}	0.82^{A}
M50	3.69^{B}	0.269^{F}	17.2^{D}	24.0^{D}	30.7^{D}	0.95^{A}
N25	4.31^{A}	0.245^{G}	9.0^{E}	15.2^{E}	21.5^{E}	0.79^{A}
N50	3.57^{BC}	0.352^{A}	4.6^{EF}	9.0^{F}	13.6^{F}	0.30^{B}
S25	3.22^{C}	0.245^{G}	0.3^{F}	6.6^{F}	13.6^{F}	0.76^{A}
S50	3.68^{B}	0.277^{D}	-11.5^{G}	-6.7^{G}	-1.9^{G}	0.98^{A}
I	Not Measured		38.7	43.2	47.3	0.96
M			35.9	40.0	43.9	0.74
N			10.7	12.6	18.4	1.27
S			-7.9	-4.6	-1.9	1.16

*C0 stands for full-sugar control; I stands for isomalt; M stands for maltitol; N stands for mannitol; S stands for sorbitol; 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol

Table 6.2. Generalized tactile and oral stickiness intensity and oral texture trajectory of samples for three glass transition midpoint temperature (T_g midpoint) ranges.

Sample T_g midpoint (°C)	**Tactile Stickiness**	**Oral Stickiness**	**Oral Texture Trajectory**		
			Initial	**Middle**	**Final**
T_g > 30 °C	Low	Low	Brittle, Crumbly	Crumbly, Cohesive	Toothpacking
15 °C < T_g < 30 °C	Low	Moderate	Brittle	Tacky, Cohesive	Toothpacking, Enveloping
T_g < 15 °C	High	High	Deformable	Stringy	Enveloping

Chapter 7: Glass transition prediction strategies based on the Couchman-Karasz equation in model confectionary systems

7.1 Abstract

Previous research highlighted the impact of sugar replacement on confectionary texture and identified the glass transition temperature (T_g) as a promising predictor of texture in amorphous confections. The utility of this relationship can be extended by the construction of a model that predicts the T_g of a mixture, T_{gm}, based on ingredient composition and final cook temperature. The Couchman-Karasz equation has been established as a model to predict T_{gm} in binary and ternary mixtures of common glass-formers and water; however, its accuracy has not been investigated for complex ingredients or cooked ingredient blends. Our objectives were to compare the Couchman-Karasz predicted T_{gm}, termed T_{CK}, to the measure T_{gm} of model confectionary systems and develop an empirical correction to improve the accuracy of the Couchman-Karasz equation. We hypothesized that T_{CK} would overestimate T_{gm} and thatΔT_{gm}^{CK}, where $\Delta T_{gm}^{CK} = T_{CK} - T_{gm}$, would increase with final cook temperature. Carbohydrate blends, consisting of a combination of two or more sweeteners among sucrose, isomalt, maltitol, sorbitol, and corn syrup solids, were boiled with water to 120, 130, 140, and 150°C. The T_{gm} of each blend was measured via DSC and compared to the original and modified Couchman-Karasz T_{CK}. T_{CK} values were calculated using experimentally measured T_g and Δc_p values for all carbohydrate ingredients and literature values for water. Carbohydrate composition ratios were assumed to be constant across the cooking process. The moisture content of samples was derived using two different methods: Karl Fischer titration, conducted for a representative subset of blends, and boiling point elevation curve generation, constructed for all carbohydrate

blends. In order to achieve the most accurate assessment of the Couchman-Karasz models, ΔT_{gm}^{CK} was calculated using moisture content values measured via Karl Fischer titration. Moisture content values estimated from boiling point elevation curves were used to relate T_{gm} and moisture content across all samples and in the construction of empirical corrections. Results showed that the original Couchman-Karasz equation fit the data better than the modified Couchman-Karasz equation; although both generally overestimated T_{gm}. Blends containing sorbitol had the largest ΔT_{gm}^{CK}. While T_{gm} varied by carbohydrate composition and moisture content, the increase in T_{gm} with decreasing moisture content was linear ($\overline{R^2}$=0.984) and consistent across all blends (4.5±0.9°C/1% moisture, wb). The increase in T_{gm} with increasing cook temperature was best described by a polynomial model ($\overline{R^2}$=0.998), but adequately described by a more generalizable linear model ($\overline{R^2}$=0.979). Application of an empirical correction based either on the moisture content or final cook temperature of the blend and the T_{CK} of the dry ingredients reduced the average ΔT_{gm}^{CK} from 20.1°C and 11.3°C for the modified and original equations, respectively, to <5.6°C. The integration of these T_g-predictive models with previous insights into the relationship between T_g and texture can enable design of confectionary texture through selection of ingredients and processing conditions.

7.2 Introduction

Thermal properties of confectionary products, including the melting temperature (T_m) of crystalline components, glass transition temperature (T_g) of amorphous components, and crystalline to amorphous ratio, significantly impact system texture and stability (Levine and

Slade 1986). Predominantly amorphous (non-crystalline, disordered solid) candies are formed by heating ingredients to a set temperature and then quickly cooling the resultant supersatured sugar solution to below the temperature range in which recrystallization of sugars can occur, between T_g and T_m of the material (Roos 1995; Hartel and others 2011). The transition from an amorphous glass to a rubber is associated with a decrease in viscosity and an increase in mobility (Roos and Karel 1991a). Therefore, amorphous food materials held above their T_g are said to be rubbery and have leathery to soft/sticky properties, while amorphous materials below their T_g are said to be glassy or crisp and are less susceptible to stickiness, deformation, crystallization or structural instability than their rubbery counterparts (Katz and Labuza 1981; Levine and Slade 1986; Roos and Karel 1991a; Slade and others 1991; Mendenhall and Hartel 2014).

The glassy amorphous state is a metastable, non-equilibrium state, and the temperature at which a material undergoes the glass transition is positively related to the molecular weight of the material or material ingredients (Slade and others 1991; Roos 1995; Hartel and others 2011). In addition to composition, T_g is impacted by moisture content and the thermal history of the sample (Abiad and others 2009). Caramelization can occur during the processing of confectionary products, significantly altering the thermal profile, as smaller molecular fragments decrease T_g, while polymerization increases T_g (Vanhal and Blond 1999). Because T_g plays a significant role in product texture and stability, accurate prediction of T_g based on formulation and processing conditions is valuable for both formula development and process control (Slade and others 1991; Abiad and others 2009).

Numerous models have been developed to predict the T_g of mixtures, T_{gm}, based on the properties of the components of the mixture. The Gordon–Taylor (Gordon and Taylor 1952) and Couchman–Karasz (Couchman and Karasz 1978) models are two of the most ubiquitous, particularly in food and food ingredient research (Orford and others 1990; Roos 1992; Arvanitoyannis and Biliaderis 1999; Pouplin and others 1999; Liu and others 2007; Chaudhary and others 2011; Ruiz-Cabrera and Schmidt 2015). Gordon-Taylor and Couchman-Karasz predicted T_g values will hereafter be written as T_{GT} and T_{CK}, respectively. The Gordon-Taylor equation (Equation 1), in which x_i is the molar or weight fraction of component i, T_{gi} is the Tg of component i, and K is a constant that is specific to the components in the mixture and related to the coefficient of expansion of the components as they undergo the glass transition, was developed to predict the T_g of polymer blends (Gordon and Taylor 1952; Truong and others 2002).

$$T_{GT} = \frac{x_1 T_{g1} + K x_2 T_{g2}}{x_1 + K x_2} \quad (1)$$

While the Gordon-Taylor equation is generally reliable in the prediction of T_g for polymer blends and polymer-plasticizer blends, it is less accurate in the prediction of Tg for systems with low molecular weight solutes (Katkov and Levine 2004). The Couchman-Karasz equation, which is based on the assumption that the glass transition is a thermodynamic event, weights the T_g of components by the change in heat capacity (ΔC_p) instead of the change in volume at the glass transition (Couchman and Karasz 1978; Abiad and others 2009). The original form of the Couchman-Karasz equation (2) includes the assumption that ΔC_p is independent of

temperature (Katkov and Levine 2004). The notation ΔC_{pi} is used to refer to the ΔC_p at the glass transition for component i.

$$\ln(T_{CK}) = \frac{\Delta C_{p1} x_1 ln(T_{g1}) + \Delta C_{p2} x_2 ln(T_{g2})}{\Delta C_{p1} x_1 + \Delta C_{p2} x_2} \quad (2)$$

The equation was modified by ten Brinke and others (1983) to Equation 3, the most commonly used form of the Couchman-Karasz equation, which assumes instead that ΔC_p is proportional to temperature.

$$T_{CK} = \frac{\Delta C_{p1} x_1 T_{g1} + \Delta C_{p2} x_2 T_{g2}}{\Delta C_{p1} x_1 + \Delta C_{p2} x_2} \quad (3)$$

The Couchman-Karasz equation is frequently extended to ternary or quaternary systems, which can be expressed in simplified form (Equation 4) or treated as a binary mixture of solids and water (Equation 5) (Truong and others 2002; Katkov and Levine 2004).

$$T_{CK} = \frac{\sum \Delta C_{pi} x_i T_{gi}}{\sum \Delta C_{pi} x_i} \quad (4)$$

$$T_{CK} = \frac{\Delta C_{p\ solids} x_{solids} T_{g\ solids} + \Delta C_{p\ water} x_{water} T_{g\ water}}{\Delta C_{p\ solids} x_{solids} + \Delta C_{p\ water} x_{water}} \quad (5)$$

More complex modifications to the Couchman-Karasz equation have been made, including the modifications by Pinal (2008), which accounts for the entropy of mixing of the components in the blend, and by Kwei (1984), which added a term to account for hydrogen bonding interaction between polymeric components; however, exploration of these models is beyond the scope of this work.

To date, most evaluations of the Couchman-Karasz equation for prediction of T_g within the food realm have focused on binary or ternary mixtures of carbohydrates, proteins, and water (Orford and others 1990; Kalichevsky and others 1992; Arvanitoyannis and others 1993; Kalichevsky and others 1993; Kalichevsky and Blanshard 1993; Gontard and Ring 1996; Pouplin and others 1999; Matveev and others 2000; Liu and others 2007; Saavedra-Leos and others 2012), though Roos (1992) has also published an investigation of the T_g of strawberries and horseradish at various moisture content and a_w values. Amorphous mixtures are generally prepared by freeze drying or dehydration of a solution (Roos and Karel 1991b; Arvanitoyannis and others 1993; Liu and others 2007; Kawai and Hagura 2012) or by melting and quick-cooling, often via DSC, (Orford and others 1990; Simatos and others 1996; Wungtanagorn and Schmidt 2001; Ruiz-Cabrera and Schmidt 2015). This study aims to provide a realistic assessment of the reliability of Couchman-Karasz models for use in full- and reduced-sugar confectionary systems, employing a method of amorphization which approximates the cooking process employed for the production of confectionary products.

One persistent challenge in use of Couchman-Karasz or other models to predict T_g is the determination of moisture content. In order to predict the T_g for model confectionary systems, our first objective was to estimate the moisture content of model confectionary systems cooked to 120, 130, 140, and 150°C, which correspond to the firm ball, hard ball, soft crack, and hard crack stages of sugar cooking, respectively. Moisture content was estimated through the generation of boiling point elevation curves and compared to moisture content values measured via Karl Fischer titration for a subset of samples. We hypothesized that moisture content at a given final cook temperature would increase with increasing moles of solute.

Our second objective was to assess the fit of the original and modified Couchman-Karasz model for model confectionary systems. We hypothesized that the Couchman-Karasz model would overestimate T_g and thatΔT_{gm}^{pred}, or the difference between the measured and predicted T_g, would increase with increasing final cook temperature, due to the heat-induced decomposition of ingredients. Finally, our third objective was to develop an empirical model to predict the T_g of model confectionary systems from the initial composition of the blend and final cook temperature. We hypothesized that the application of this empirical correction would result in a reduction of the average ΔT_{gm}^{pred}.

7.3 Materials and methods

Model confectionary system ingredients and formulation

Simplified model confectionary systems, comprised only of carbohydrates and water, were developed. Carbohydrate ingredients utilized include cane sucrose (C & H Sugar, ASR Group, West Palm Beach, FL), corn syrup solids (Dextrose Equivalent 49-55, supplier requests nondisclosure), isomalt (CK Products, LLC, Fort Wayne, IN), maltitol (supplier requests nondisclosure), and sorbitol (supplier requests nondisclosure). The typical carbohydrate profile of the corn syrup solids were as follows: 8% dextrose, 56% maltose, 16% maltotriose, and 20% higher saccharides. Carbohydrate blends were formulated to span the range of sugar to corn syrup ratios and sugar alcohol usage levels of model caramel coating systems described in Chapter 4.

Sugar alcohols were introduced into the model confectionary systems at 20 and 40% of the total carbohydrate mass, usage levels which are similar to 25 and 50% replacement of

sugars in confectionary systems. One sugar alcohol at most was used in each blend. The specific sugar alcohol used and the usage level is abbreviated in sample naming schemes as follows: C0 for control or no sugar alcohol used, I for isomalt, M for maltitol, S for sorbitol, 20 for 20% sugar alcohol by total solids mass, and 40 for 40% sugar alcohol by total solids mass. Three sucrose to corn syrup ratios were utilized: 1 to 0, 3 to 1, and 1 to 1. These ratios are indicated in formula names by the abbreviation CS and the numbers 0, 25, or 50, which describe the percentage of corn syrup out of the total mass of corn syrup and sucrose. All combinations of sugar alcohol, sugar alcohol usage level, and corn syrup solids usage level were produced with the exception of the 100% sucrose formula. The percent composition and sample code names for carbohydrate blend formulas are displayed in Table 7.1.

Model confectionary system preparation

To prepare the samples, carbohydrate ingredients in the ratios described in Table 7.1 and totaling 500g per batch were weighed and mixed with 200g of filtered water in a stainless steel saucepan. The temperature of the mixture was monitored with a high accuracy Traceable® thermocouple (Thermo Fisher Scientific Company, Waltham, Massachusetts, U.S.A.) and stirred continuously as it was heated on a gas range. Approximately 50g of material was removed from the pan at 120, 130, 140, and 150°C and deposited in droplets on an aluminum foil grid, for use in thermal analysis, and poured into a silicon mold (WOOTOP, Shenzhen, Guangdong, China), for use in moisture analysis. Droplets were sealed in pans for thermal analysis within 2 hours of sample preparation in order to minimize changes to the moisture content of the material prior to analysis. Material reserved for moisture content analysis was stored in a freezer to preserve the physical state and moisture content of the samples. Each formula was produced once, with

the exception of three representative samples, I40-CS25, M40-CS25, and S40-CS25, which were produced twice in order to evaluate the reproducibility of the preparation process. Data from both batches of representative samples, I40-CS25, M40-CS25, and S40-CS25, were used exclusively in the comparison of moisture content values obtained via boiling point elevation estimation and Karl Fischer titration, presentation of representative DSC thermograms, and assessment of the fit of Couchman-Karasz equations to experimental data; data from the first batch of all samples was to generate boiling point elevation curves and to construct empirical equations.

Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) was conducted to characterize the glass transition of behavior of carbohydrate ingredients and model confectionary systems. All runs were conducted using a DSC Q2000 instrument with an autosampler (TA Instruments, New Castle, DE, U.S.A.) and a refrigerated cooling system (RCS 90). The instrument was calibrated using an indium reference (known melting temperature of 156.6°C; known enthalpy of 28.71 J/g) prior to analysis. All samples were massed in Tzero pans and sealed with hermetic lids (TA Instruments, New Castle, DE, U.S.A.), and runs were carried out under a dry nitrogen purge gas at a flowrate of 50mL/min. Glass transition temperature (T_g) onset, midpoint, and endpoint values, as well as change in specific heat capacity at the glass transition (Δc_p) were determined from DSC thermograms using the Glass/Step Change function with Manual Tangent Selection within Universal Analysis software (Version 4.4A, TA Instruments New Castle, DE, U.S.A.).

With the exception of the corn syrup solids, all carbohydrate ingredients were originally in the crystalline state. Therefore, prior to analysis of T_g properties, crystalline carbohydrate ingredients were made amorphous using a melting and quick cooling protocol in the DSC. Crystalline ingredient samples (8.9 $\pm$ 0.8 mg) were heated at a rate of 10°C/min until just melted, to a temperature of 200°C, 160°C, 155°C, and 105°C, for cane sucrose, isomalt, maltitol, and sorbitol, respectively. Melted sucrose, isomalt, maltitol, and sorbitol samples were then quickly cooled to -50°C and heated again at 10°C/min to 220°C, 180°C, 175°C, and 125°C, respectively, to capture the glass transition and confirm the complete amorphization of samples. The glass transition parameters of the corn syrup solids ingredient were measured by equilibrating the already amorphous sample (8.2 $\pm$ 0.2mg) at -60°C and then scanning at a rate of 10°C/min to 95°C. The T_g of isomalt, maltitol, sorbitol, and corn syrup solids was measured in duplicate, and the T_g of sucrose was measured in triplicate. The T_g data for isomalt, maltitol, and sorbitol presented in this study were previously reported (Chapters 4 and 6).

Model confectionary systems were made amorphous by the cooking process described in the methods section on model confectionary system preparation. To facilitate loading of samples, which were often sticky and hard to handle, into Tzero pans, samples droplets were deposited onto within 5 x 5mm squares on a sheet of aluminum foil. The foil squares were then cut out using a precision blade, and samples were loaded with foil into pans. The mass of a 0.25mm^2 square of foil was taken into account in the determination of sample mass, and a reference pan containing a 0.25mm^2 square of foil was used to produce the baseline for all sample runs. The T_g parameters of model confectionary samples (10.7 $\pm$ 5.7mg) cooked to 120,

130, 140, and 150°C were measured in duplicate using a protocol of equilibration at -60°C, after which samples were heated at a rate of 10°C/min to 95°C.

Model confectionary system boiling point elevation curve generation

Boiling point elevation curves were generated for each ratio of sucrose, corn syrup solids, and sugar alcohol previously described in Table 7.1. A total of 60g of solids was combined with 40g of filtered water in a 100ml beaker. The beaker and contents were heated on a Corning PC-420D hot plate (Corning Inc., Corning, New York, U.S.A.). The mixture was stirred continuously with a spatula and the temperature was monitored with a high accuracy Traceable® thermocouple (Thermo Fisher Scientific Company, Waltham, Massachusetts, U.S.A.). The initial mass of the beaker was tared and the mass was recorded with a Mettler PM6000 scale (Mettler Toledo, Columbus, Ohio, U.S.A.) at increments of 2°C starting at 100°C and continuing until the mass of the mixture reached the mass of the initial solids content (60g). This process was completed once for every formula, and repeated a second time for three representative samples (I40-CS25, M40-CS25, S40-CS25) to evaluate the reproducibility of the method.

The initial solids mass fraction in each test was 0.60. All mass lost during heating was assumed to be water, and the solids mass fraction was calculated as the quotient of the initial mass of solids (60g) divided by the total mass of solids and water at a given temperature. Following data collection, boiling point elevation curves showing the change in boiling point over a range of solid mass fraction values for individual formulas and averaged curves for aggregated data of like-formulas were produced in Microsoft excel (Microsoft Corporation,

Seattle, WA, U.S.A.). Curves for formulas with like corn syrup solids composition represent an average of 6 curves for CS0 or 7 curves for CS25 and CS50, while curves for formulas with like sugar alcohol composition represent an average of 3 curves each.

Karl Fischer titration

Moisture content values for a representative subset of the samples (I40-CS25, M40-CS25, S40-CS25) were determined by volumetric Karl Fischer titration (EMD, Aquastar AQV21). The analysis was conducted by DonLevy Laboratories (Crown Point, Indiana, U.S.A.), and measurements were made in duplicate for each final cook temperature (120, 130, 140, and 150°C) for two batches of each of the three formulas. A 50% formamide, 50% methanol solvent system was used for all testing. Samples were stirred continuously in the solvent system for 5 minutes to dissolve the sample; then the solution was titrated for approximately 10 min. The analysis was conducted at ambient conditions of 20.0% relative humidity and 23.0°C.

Modeling of glass transition data

Linear and polynomial empirical models relating sample T_g to sample moisture content and cook temperature, as well as R^2 values for each model, were generated from T_g and moisture content data from the first batch or trial of each model confectionary formula using Microsoft excel (Microsoft Corporation, Seattle, WA, U.S.A.).

7.4 Results and discussion

Glass transition properties of ingredients

The average measured T_g onset, midpoint, and endpoint values, as well as the Δc_p, of carbohydrate ingredients used in this study are reported in Table 7.2. In general, the expected

positive correlation between molar mass and T_g is observed. The exception to this trend is seen for corn syrup solids, which have a higher average molar mass than sucrose, but a lower T_g. This may be due to plasticization of higher molecular weight carbohydrates in the corn syrup solids by monosaccharides and small amounts of residual water not removed in the manufacturing process. The measured T_g midpoint of sucrose, 70.4°C, falls in the range of previously reported T_g values also measured at 10°C/min (69.7°C to 72.2°C) (Orford and others 1990; Vanhal and Blond 1999; Liu and others 2007; Lee and others 2011). Measured T_g midpoint values were lower than some previously reported literature values for isomalt (measured 43.2°C, literature 59.5°C (Cammenga and Zielasko 1996), maltitol (measured 40.0°C, literature 50.3°C (Lappalainen and Pitkänen 2006), and sorbitol (measured -4.6°C, literature -1.6°C (Yu and others 1998). Differences in measured and previously reported T_g values for sugar alcohol ingredients may be due to differences in ingredient processing and properties between suppliers.

In order to most accurately reflect the glass transition properties of the specific ingredients used, the experimentally measured midpoint T_g and Δc_p values shown in Table 7.2 were used throughout for the calculation of T_{CK}. Glass transition properties for water were not measured in this study. The values of T_g reported in the literature for water range from 135K to 143K (Sugisaki and others 1968; Macfarlane and Angell 1984; Hallbrucker and others 1989); in this study, a T_g of 136K (-137°C) and a Δc_p of 1.94 J/g/°C were used for all calculations (Katkov and Levine 2004).

Boiling point elevation curves

Figure 7.1A shows that boiling point elevation in the model confectionary systems studied was inversely related to corn syrup concentration. Differences between CS0 and CS25 formulas were minimal, but moisture content of CS0 formulas exceeded that of CS50 formulas by an average of 1.1% (wet basis) at a given temperature. This relationship is intuitive, as boiling point is a colligative property, and higher usage levels of corn syrup solids, which have a higher average molecular weight than the other carbohydrates studied, would result in fewer total moles of solute and less elevation of the boiling point. This trend also agrees with previously published comparisons of boiling point elevation curves for corn syrup and sucrose solutions (Hartel and others 2011).

When average boiling point elevation curves for each sugar alcohol treatment (Figure 7.1B) were compared, however, consistent trends did not emerge. Because isomalt and maltitol have similar molecular weights to sucrose, while the molecular weight of sorbitol is approximately half that of sucrose, the expectation was that samples containing sorbitol would exhibit greater boiling point elevation than blends containing isomalt or maltitol, and that the samples composed of 40% sorbitol would exhibit greater boiling point elevation than the samples containing only 20% sorbitol. Instead, while the S20 samples did exhibit the greatest degree of average boiling point elevation, the averaged S40 samples exhibited a relatively low degree of boiling point elevation. While this result is counterintuitive, it is important to note that no clear separation of boiling point elevation curves by sugar alcohol treatment is observed. Some spread can be seen at lower temperatures, but curves tended to converge after 120°C. Between temperatures of 120°C to 150°C, the maximum difference in average moisture

content between samples of different sugar alcohol treatments was 1.7% (wet basis). While the variation in boiling point observed between formulas was relatively small, a 1% difference in moisture content can have a significant impact on T_g, as well as other material properties. Further study and isolation of single formula variables should be conducted to confirm and explain trends in boiling point elevation of model confectionary systems.

Moisture content of model confectionary samples

Generation of boiling point elevation (BPE) curves provided a simple means of estimating moisture content, but does not give a direct measurement of sample moisture content. Karl Fischer (KF) titration is generally considered the most accurate method of moisture content determination for low-moisture food materials, due to its relatively low limits of detection, and for carbohydrate materials, which are prone to decomposition during heating, and therefore, prone to systematic error when gravimetric methods are used (Ruiz 2005). In order to assess the accuracy of the BPE estimation method, KF titration was performed and measured moisture content was compared to estimated values for a representative subset of samples, I40-CS25, M40-CS25, and S40-CS25 (Table 7.3).

In general, BPE estimated and KF measured moisture content values fell within 1% moisture content, wet basis (wb), of each other for samples cooked to 120 or 130°C, but values diverged for samples cooked to 140 or 150°C. For all samples, KF measured moisture content values were higher than BPE estimated values for the two higher final cook temperature. In I40-CS25 and S40-CS25 samples cooked to 150°C, the difference between KF measured and BPE estimated moisture content values was close to 3%, wb. Since the difference in moisture

content values between the methods increases with cook temperature, it is probable that the difference is due to non-water volatile losses during the heating of samples in the BPE method. It is worth noting that while consistent differences are found between moisture content values determined by the KF and BPE methods, only minor differences are found for KF measured moisture content values between samples. KF measured moisture content values for S40-CS25 samples exceed values for I40-CS25 and M40-CS25 samples by an average of 0.67, 0.39, 0.12, and 0.31% wb, when heated to 120, 130, 140, and 150°C, respectively.

Glass transition properties of model confectionary systems

Representative DSC thermograms for I40-CS25, M40-CS25, and S40-CS25 samples cooked to 120, 130, 140, and 150°C are presented in Figure 7.2. The small endothermic peak in Figure 7.2A can be attributed to enthalpic relaxation that occurred in the I40-CS25 sample cooked to 150°C between sample production and DSC analysis. Comparison between plots shows a decrease in T_g from I40-CS25 to M40-CS25 to S40-CS25, corresponding to the decrease in T_g from isomalt to maltitol to sorbitol (Table 7.2). Comparison of thermograms within each plot shows a consistent increase in T_g with increasing cook temperature, which is intuitive due to the decrease in moisture content with increasing cook temperature. These effects of cook temperature and sugar alcohol treatment were maintained across all samples; however, corn syrup solids content had an inconsistent effect on T_g. DSC data for all samples can be found in Appendix D.

Assessment of fit of Couchman-Karasz equations to experimental T_{gm}

Experimental T_{gm} data for I40-CS25, M40-CS25, and S40-CS25 samples are plotted alongside T_{CK} values calculated via the original and modified Couchman-Karasz equations at a range of solid weight fraction values (Figure 7.3). Comparison of TCK for both versions of the Couchman-Karasz equation shows that the models are nearly identical when the solids weight fraction approaches 1, but diverge as the solids weight fraction decreases. This visual juxtaposition of experimental data with T_{CK} from the original and modified Couchman-Karasz equations, Equation 2 and Equation 3, respectively, allow for a comparative assessment of fit for both models. The modified T_{CK} overestimates T_{gm} for all three samples, while the original T_{CK} overestimates T_{gm} for S40-CS25 samples, but comes close to T_{gm} for I40-CS25 and M40-CS25 samples (±5°C). Table 7.4 provides numerical values for T_{gm} and T_{CK}, calculated using the original and modified Couchman-Karasz equations. When the original Couchman-Karasz equation was used, mean values of T_{gm} for I40-CS25 and M40-CS25 fell within 5.5°C of the calculated T_{CK} values. However, though the original Couchman-Karasz comes close to T_{gm} for I40-CS25 and M40-CS25 samples, it overestimated mean values of T_{gm} for S40-CS25 samples by 10 to 12°C. Further, though the original Couchman-Karasz equation T_{CK} is within 5.5°C of T_{gm} for the range of solid mass fraction values studied, it is evident that the measured T_{gm} decreases with increasing moisture content at a greater rate than predicted by either equation.

Figure 7.4 provides a visual representation of this trend. We originally hypothesized that ΔT_{gm}^{pred} would increase with increasing cook temperature, as heat-induced decomposition of carbohydrates has been shown to result in a lowering of the average molecular weight and T_g of the sample (Jiang and others 2008). However, as Figure 7.4 shows, the opposite effect of cook

temperature on ΔT_{gm}^{pred} is observed: the degree to which T_{CK} overestimates T_{gm} decreases with increasing cook temperature. While this result was at first surprising, it agrees with past research which found that the plasticizing effect of water is not directly proportional to moisture content. Instead, the degree of plasticization due to water increases more rapidly at higher water concentrations due to an increase in free volume and mobility in the system (Lechuga-Ballesteros and others 2002; Abiad and others 2009). It can be concluded, then, that the effect of decomposition due to cooking has a small effect on T_{gm} relative to the plasticizing effect of water in these systems within the temperature and moisture content ranges studied. It is likely that the effect of decomposition would dominate in samples cooked above 150°C, as the residual moisture content becomes very small and the rate of decomposition increases.

Development of empirical corrections to Couchman-Karasz equation

The modified Couchman-Karasz equation (Equation 3), the most commonly used form of the equation (Katkov and Levine, 2004), failed to reliably predict T_{gm} of the model confectionary systems studied. The original Couchman-Karasz equation (Equation 2) came close for some, but not all, samples, and showed a systematic shift from under to overestimation of T_{gm} as moisture content increased. In order to develop an empirical model that can predict T_{gm} with greater reliability for this sample set, experimental T_{gm} values were compared to both estimated sample moisture content (Figure 7.5) and final cook temperature (Figure 7.6).

Figure 7.5 shows that T_{gm} decreases linearly with increasing moisture content ($\overline{R^2}$=0.984) at a fairly consistent rate of 4.5±0.9°C for every 1.0% change in moisture content (wb). The linear equations and R^2 values for each individual formula are given in Appendix E.

Because the slope of the relationship between T_{gm} and moisture content appears to be relatively independent of formula, it is reasonable to develop a standardized empirical model for the estimation of T_{gm} by moisture content. While the rate of change in T_{gm} with moisture content was formula-independent, the absolute T_{gm} at a given moisture content was strongly dependent on formula. It was therefore logical to develop the empirical model as a correction to the Couchman-Karasz equation, using the calculated T_{CK} value for solids and applying the empirical relationship between T_{gm} and moisture to adjust for changes in moisture content. The resultant equation (Equation 6), in which x is equal to the % moisture (wb) and $T_{CK_{solids}}$ is the calculated T_g for only the non-water components of the sample, can be used to calculate a new T_{CK}^{MC}. The superscript MC refers to the input variable, Moisture Content, in this empirical equation. Since the original and modified versions of the Couchman-Karasz equation give nearly identical results when moisture content approaches 0, the more commonly-used and mathematically simpler modified version was used to calculate $T_{CK_{solids}}$.

$$T_{CK}^{MC} = T_{CK_{solids}} - 4.48x - 19 \quad (6)$$

Comparison of T_{CK}^{MC} to measured T_{gm} values showed that the use of the empirical correction improved the overall accuracy of Couchman-Karasz equation, from an average ΔT_{gm}^{CK} of 20.1°C and 11.3°C for the modified and original equations, respectively, to an average $\Delta T_{gm}^{CK^{MC}}$ of 5.5°C across all samples. This improvement was promising, but calculation of T_{CK}^{MC} still requires measurement of moisture content, which can be challenging for model confectionary systems or other carbohydrate-based systems. To address this challenge, a second approach to the development of an empirical correction was taken, this time using final

cook temperature instead of moisture content as the empirical input variable. As Figure 7.6 shows, the absolute T_{gm} for a given cook temperature is again dependent on formula, while the increase in T_{gm} with increasing cook temperature is fairly consistent across samples. However, while the relationship between T_{gm} and cook temperature is consistent, it does not appear to be linear. The non-linear nature of the relationship between cook temperature and T_{gm} makes intuitive sense; reduction in moisture content with increasing cook temperature is the driving force for the increase in $T_{gm,}$ and moisture loss with cook temperature is likewise non-linear.

A second order polynomial equation was fit to the data and described the relationship between T_{gm} and cook temperature very well, with an average R^2 of 0.998. However, there was a considerable range in coefficients of the polynomial equation between samples. For this reason, a linear equation was also generated for the data (Appendix F). The linear models did not show as good a fit to the experimental data, but the average R^2 was still quite high (0.979) and the slope of the linear trendline was more consistent across samples (1.28±0.21°C). Polynomial and linear equations and R^2 values for individual formulas are given in Appendix E.

The averaged polynomial and linear relationship between cook temperature and T_{gm} were used to construct Equations 7 and 8, respectively, in which $T_{CK_{solids}}$ is again the calculated T_g for non-water components of the sample formula, and x is now equal to the temperature (T), in °C, above 120°C to which the sample has been heated (x = T - 120°C).

$$T_{CK}^{CT_p} = T_{CK_{solids}} - 0.0175x^2 + 1.81x - 62 \quad (7)$$

$$T_{CK}^{CT_l} = T_{CK_{solids}} + 1.28x - 60 \quad (8)$$

The superscript CT in Equations 7 and 8 refers to the new input variable, Cook Temperature, and the subscripts on CT refer to the use of either a polynomial (p) or linear (l) model. Applying these empirical corrections results in a reduction of ΔT_{gm}^{CK}; the average $\Delta T_{gm}^{CK^{CT}}$ when Equation 7 or 8 is used is 5.24 and 5.33°C, respectively.

7.5 Conclusions

Experimental T_{gm} values aligned more closely to the original Couchman-Karasz model than to the modified Couchman-Karasz model for the model confectionary systems studied, though both models overestimated T_{gm} in sorbitol-containing samples and at higher moisture content ranges. The empirical corrections developed herein provided enhanced prediction of model confectionary system T_g relative to the modified and original Couchman-Karasz equations alone. To our knowledge, this study includes the first reported empirical model for the prediction of T_g based on a processing parameter, cook temperature. The average increase in T_{gm} with decreasing moisture content or increasing cook temperature, which were found to be fairly uniform across the confectionary model systems, could provide a useful “rule of thumb” in the planning of changes to formulation or processing parameters. This applicability of the developed empirical models to systems beyond those described in this study is unknown, however, the approach utilized could easily be extended to other types of food systems.

7.6 References

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7.7 Figures and tables

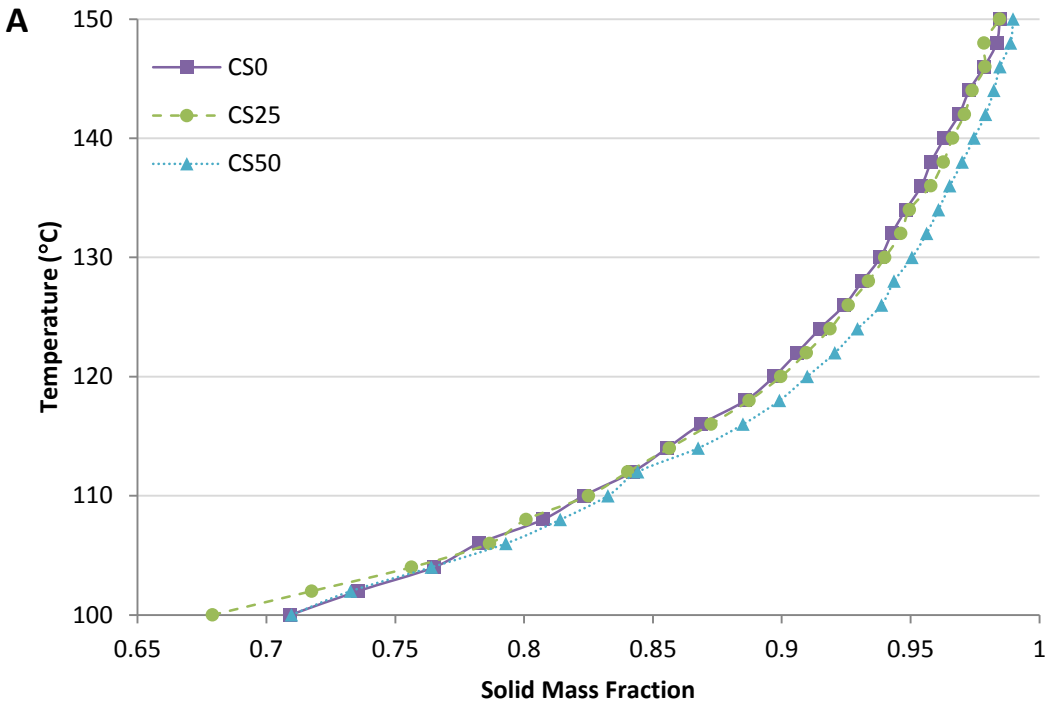

Figure 7.1. Boiling point elevation curves representing the average relationship between the temperature to which the mixture had been cooked and the solids mass fraction of the mixture, aggregated for samples with like corn syrup solids composition (A) and sugar alcohol composition (B). Formula code names are defined in Table 7.1.

B

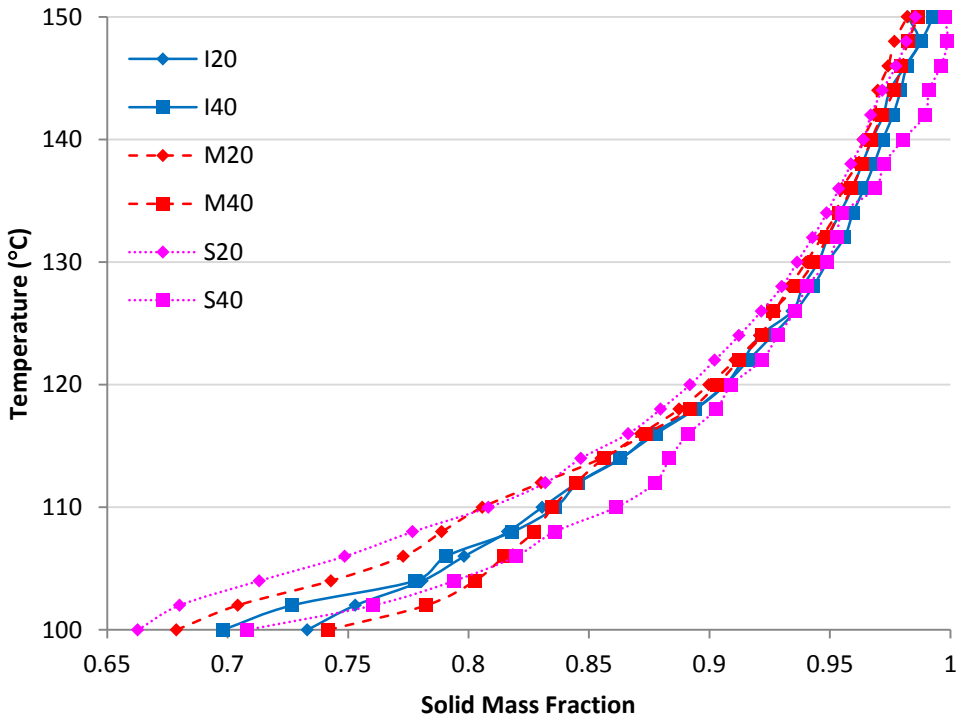

Figure 7.1 (cont.)

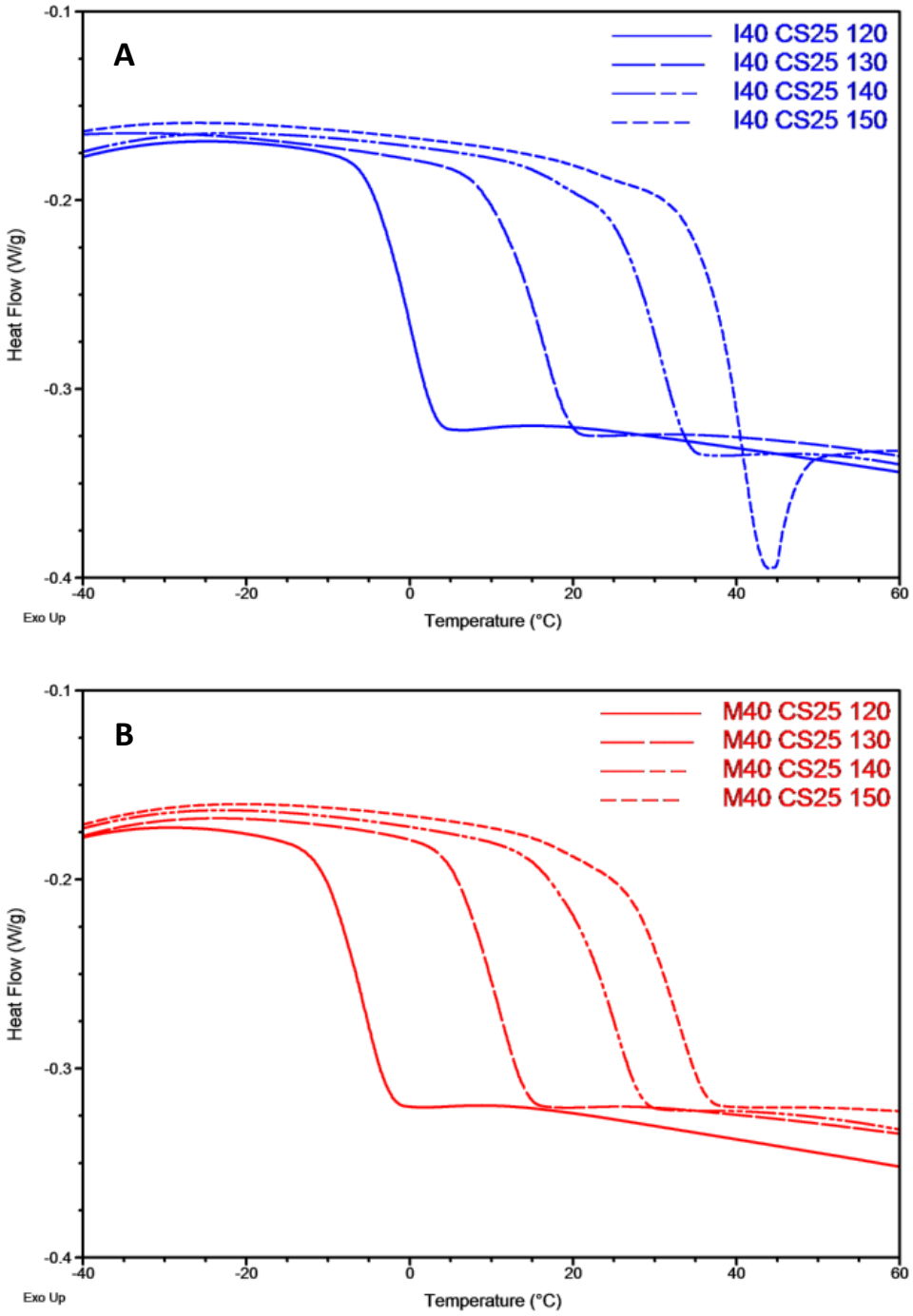

Figure 7.2. Differential scanning calorimetry (DSC) thermograms showing the glass transition region for I40-CS25 (A), M40-CS25 (B), and S40-CS25(C) samples heated to 120, 130, 140, and 150°C. Samples identities are indicated in the legends by the formula name followed by the temperature to which the sample was cooked in °C. Formula code names are defined in Table 7.1.

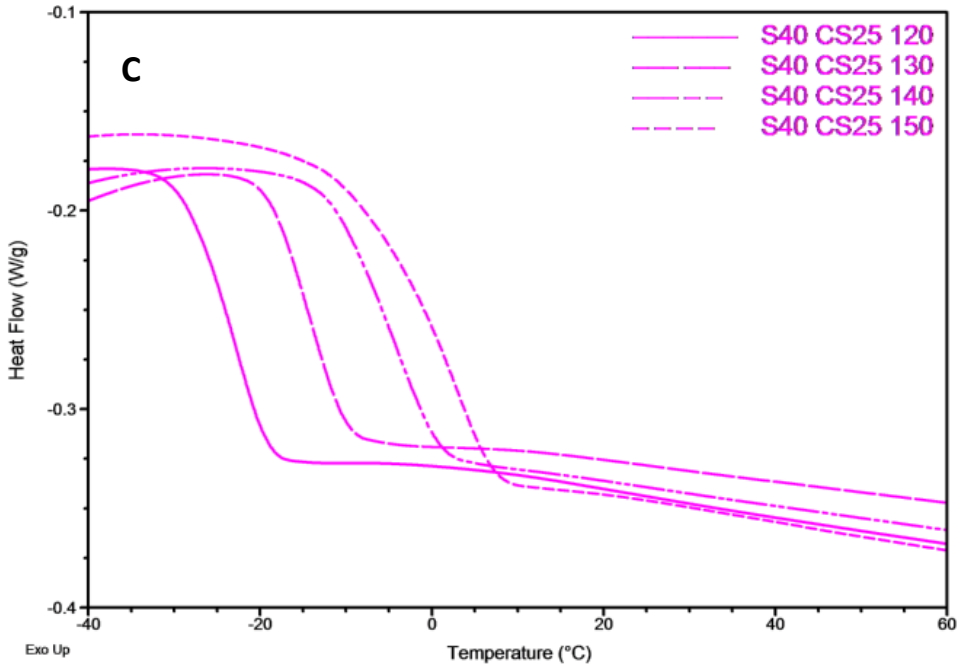

Figure 7.2 (cont.)

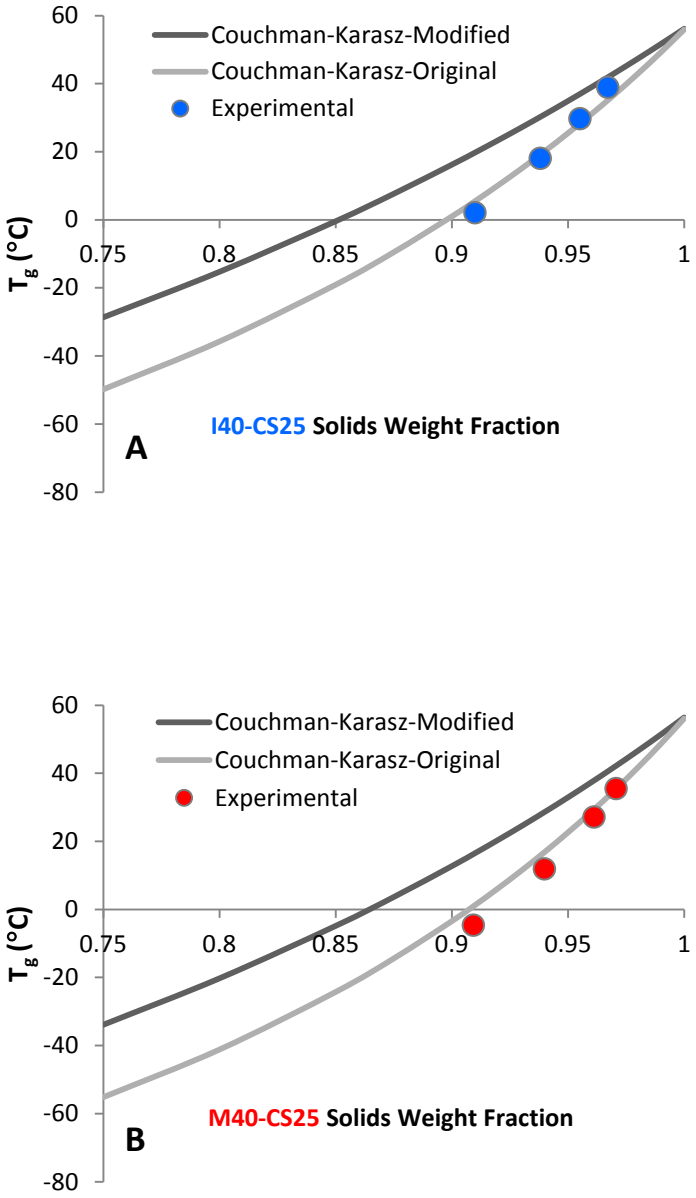

Figure 7.3. Average experimentally measured T_{gm} values plotted against average solids weight fraction, calculated as the total weight minus the weight fraction of water measured via Karl Fischer titration, across both batches for I40-CS25 (A), M40-CS25 (B), and S40-CS25 (C) samples. Experimental data is plotted with predicted T_{CK} curves obtained using both the original and modified Couchman-Karasz equations for the given formulas and at solid weight fraction values between 0.75 and 1.0. Formula code names are defined in Table 7.1.

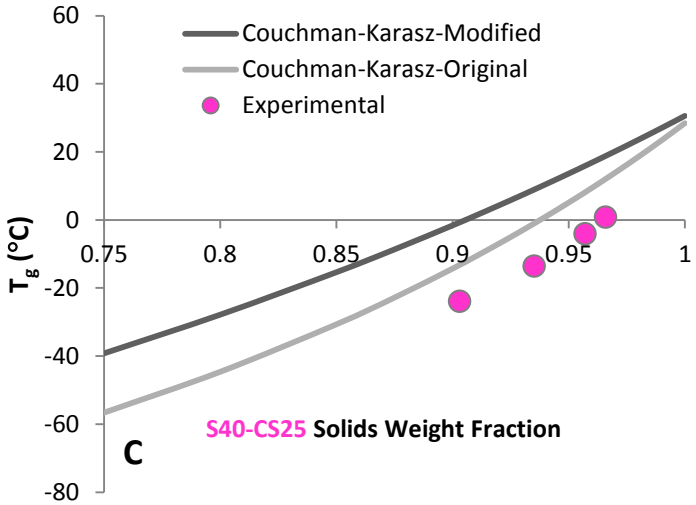

Figure 7.3 (cont.)

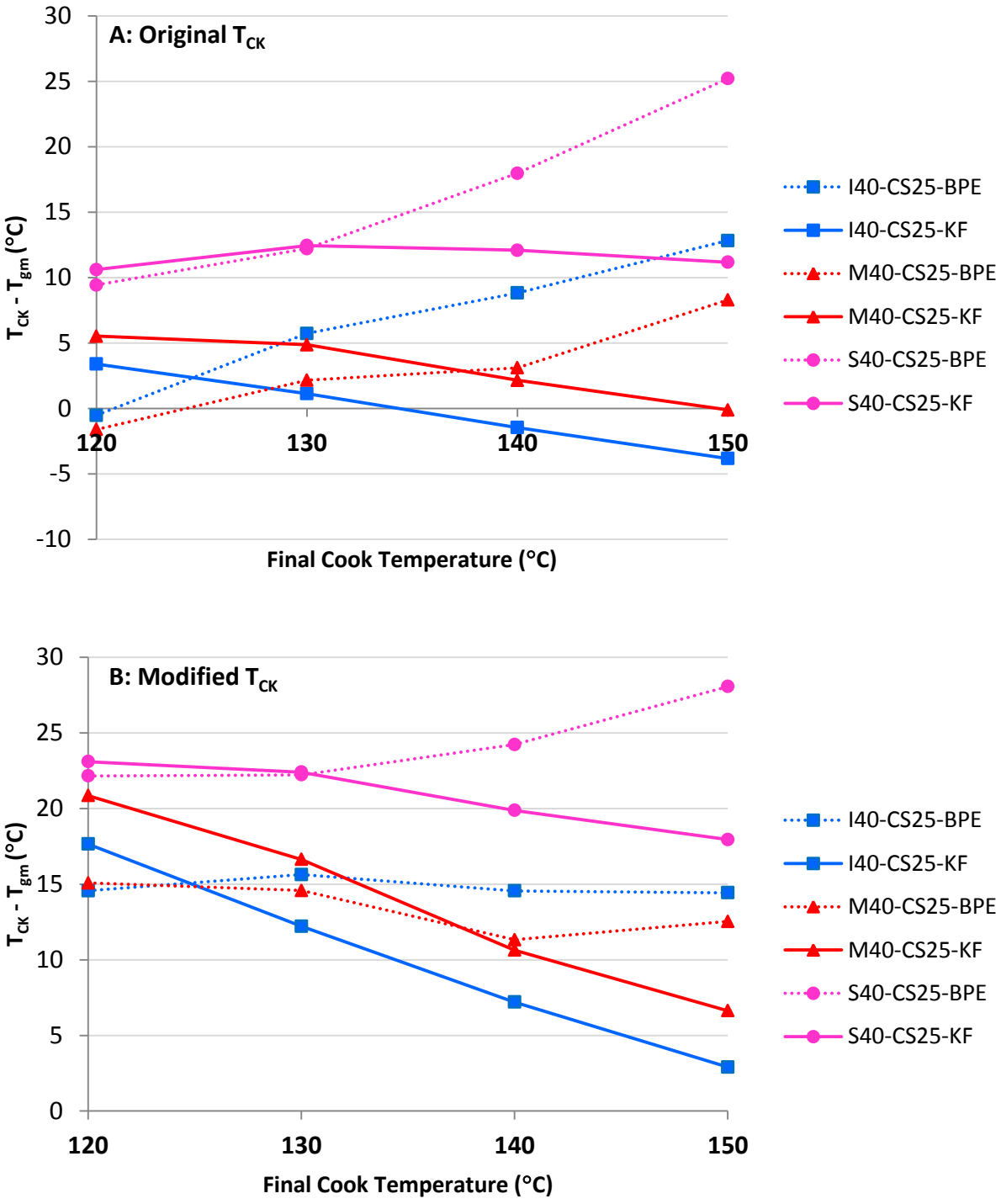

Figure 7.4. Difference between calculated T_{CK} and experimentally measured T_{gm}, by both original (A) and the modified (B) Couchman-Karasz equation and using moisture content values estimated from boiling point elevation (BPE) curves and measured via Karl Fischer (KF) titration for I40-CS25, M40-CS25, and S40-CS25 samples plotted by final cook temperature. Formula code names are defined in Table 7.1.

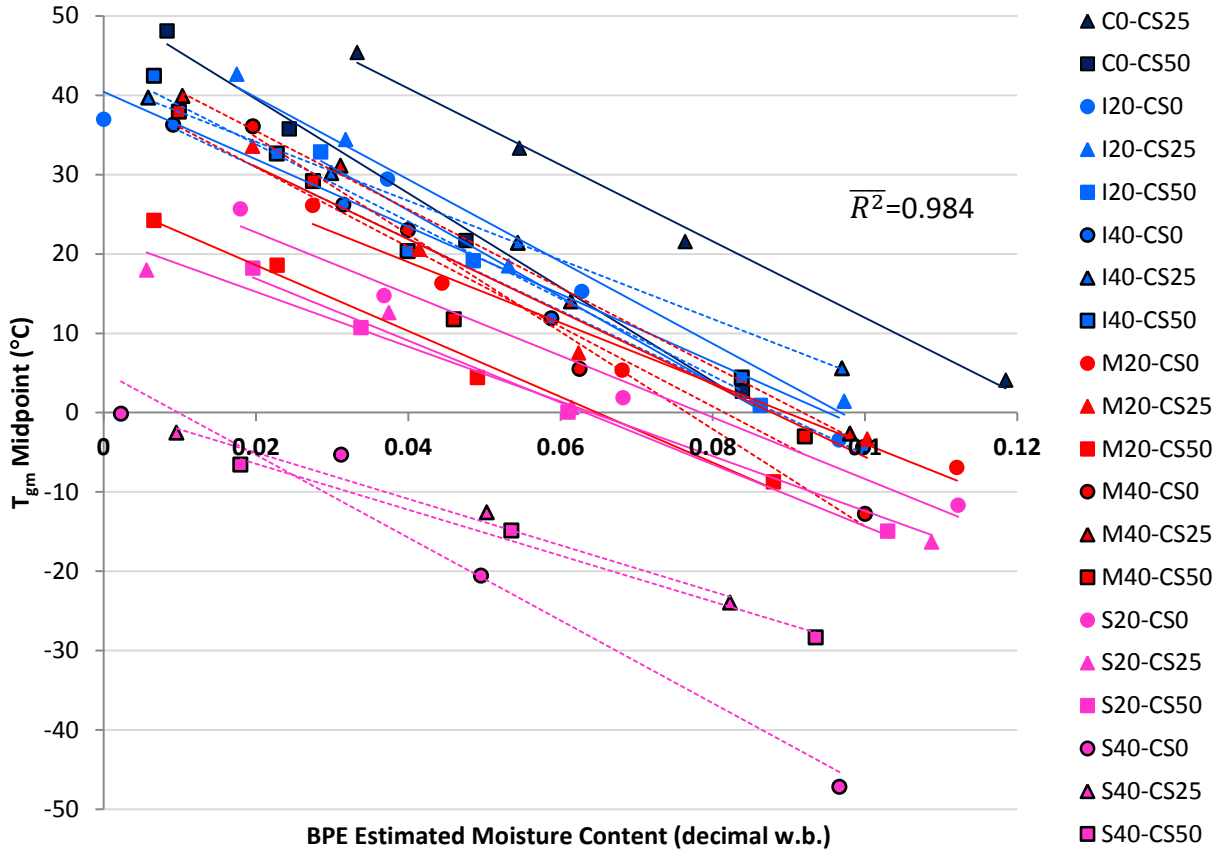

Figure 7.5. Plot of average measured T_{gm} midpoint values versus boiling point elevation (BPE) estimated moisture content, wet basis (wb), for all samples. The average R^2 for the linear trendline of each sample is given. Solid trendlines correspond to 20% sugar alcohol formulas, while dashed trendlines correspond to 40% sugar alcohol formulas. Formula code names are defined in Table 7.1.

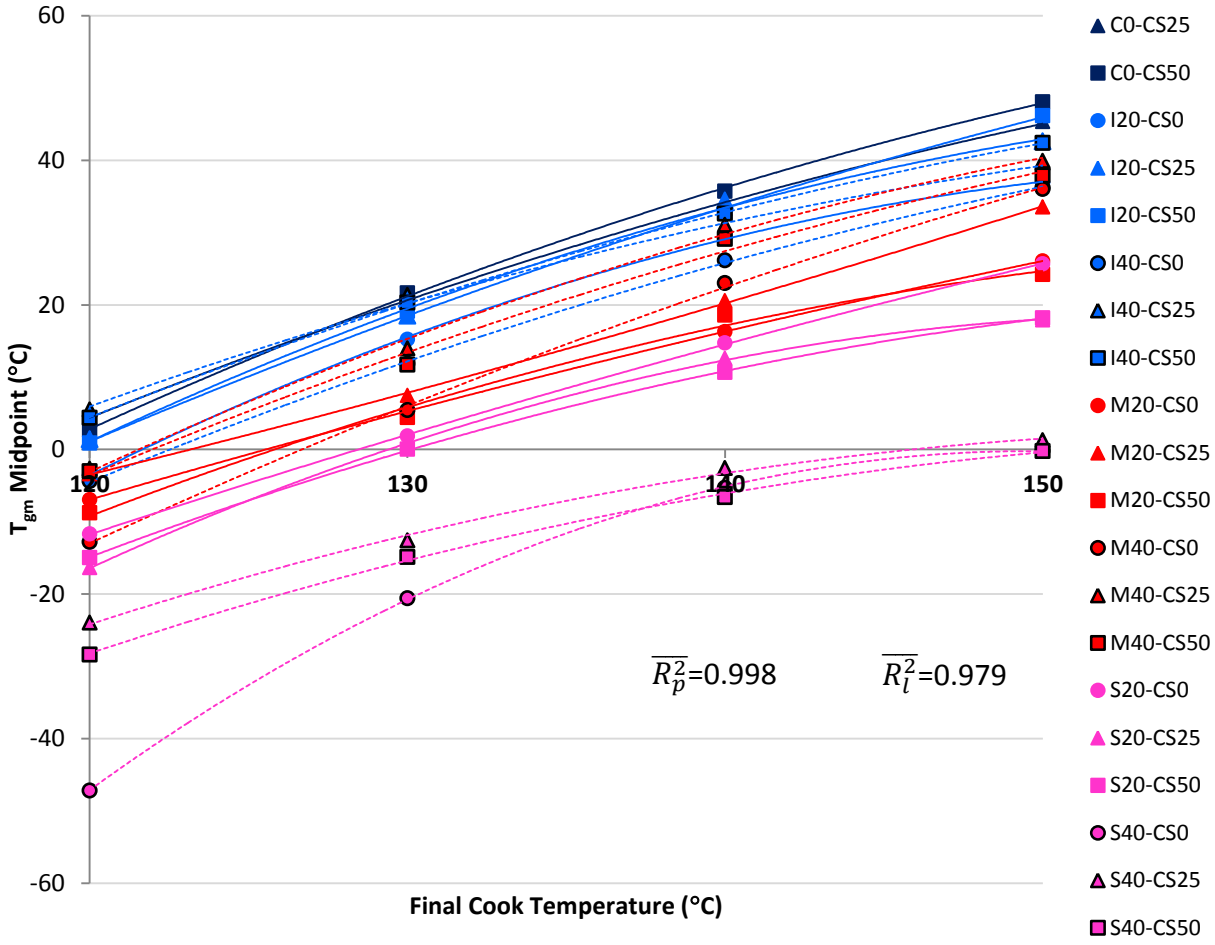

Figure 7.6. Plot of average measured T_{gm} midpoint values versus final cook temperature for all samples. Polynomial trendlines are used in this figure; an alternate figure with linear trendlines is available in Appendix F. The average R^2 for the polynomial (R_p^2) and linear (R_l^2) trendline of each sample is given. Solid trendlines correspond to 20% sugar alcohol formulas, while dashed trendlines correspond to 40% sugar alcohol formulas. Formula code names are defined in Table 7.1.

Table 7.1. Relative composition of ingredients and sample code names for model confectionary blends. Formulas are organized by % of the total mass contributed by sugar alcohol, as noted in the top row, and ratio of sucrose to corn syrup solids (CS), as noted in the second row.

	Full Sugar Formulas		**20% Sugar Alcohol Formulas**			**40% Sugar Alcohol Formulas**		
Sucrose : CS ratio	**3:1**	**1:1**	**No CS**	**3:1**	**1:1**	**No CS**	**3:1**	**1:1**
Ingredient	**% Composition**		**% Composition**			**% Composition**		
Sucrose	75	50	80	60	40	60	45	30
Corn Syrup Solids	25	50	0	20	40	0	15	30
Sugar Alcohol	0	0	20	20	20	40	40	40
Sugar Alcohol	**Sample Code Name**							
Control (none used)	C0-CS25	C0-CS50	Not Applicable			Not Applicable		
Isomalt	Not Applicable		I20-CS0	I20-CS25	I20-CS50	I40-CS0	I40-CS25	I40-CS25
Maltitol			M20-CS0	M20-CS25	M20-CS50	M40-CS0	M40-CS25	M40-CS25
Sorbitol			S20-CS0	S20-CS25	S20-CS50	S40-CS0	S40-CS25	S40-CS25

Table 7.2. Molar mass, measured T_g onset, midpoint, and endpoint, and data Δc_p values for carbohydrate ingredients, and literature values for water.

Ingredient	Molar Mass (g/mol)	T_g onset (°C)	T_g midpoint (°C)	T_g endpoint (°C)	Δc_p (J/g/°C)
C&H Cane Sucrose	342.3	66.9	70.4	73.7	0.73
Corn syrup solids	420.1*	57.1	59.0	60.9	0.76
Isomalt	344.3	38.7	43.2	47.3	0.96
Maltitol	344.3	35.9	40.0	43.9	0.74
Sorbitol	182.2	-7.9	-4.6	-1.9	1.16
Water	18.0		-137.2†		1.94†

*Average molar mass estimated from manufacturer composition specifications; †literature values from Katkov and Levine, 2004

Table 7.3. Estimated moisture content from an average of two boiling point elevation (BPE) curves and average measured moisture content from 2 Karl Fischer (KF) measurements on each of two batches of I40-CS25, M40-CS25, and S40-CS25 samples cooked to 120, 130, 140, and 150°C. Moisture content values are reported in percent wet basis (% wb). Reported standard deviation values (SD) reflect the variation in boiling point elevation curves and variation between batch averages of Karl Fischer measurements. Formula code names are defined in Table 7.1.

		I40-CS25		M40-CS25		S40-CS25	
Temperature (°C)		**BPE % wb**	**KF % wb**	**BPE % wb**	**KF % wb**	**BPE % wb**	**KF % wb**
120	Mean	9.87	9.00	10.60	9.07	10.04	9.71
	SD	0.23	0.57	1.13	0.63	2.57	0.05
130	Mean	5.32	6.19	6.50	6.01	6.55	6.49
	SD	0.17	0.65	0.51	0.47	2.15	0.31
140	Mean	2.71	4.49	3.73	3.88	2.98	4.30
	SD	0.41	0.01	0.87	0.58	2.87	0.30
150	Mean	0.61	3.29	1.68	2.93	0.47	3.42
	SD	0.04	0.17	0.91	0.60	0.67	0.08

Table 7.4. Mean experimental T_{gm} midpoint and standard deviation (SD) values, and original and modified T_{CK} values, calculated using Karl Fischer mean moisture content values, for I40-CS25, M40-CS25, and S40-CS25 samples cooked to 120, 130, 140, and 150°C. Experimental data presented are drawn from two batches for each model confectionary formula. Formula code names are defined in Table 7.1.

		Experimental T_g		**Couchman-Karasz T_g**	
Formula	**Temperature (°C)**	**T_{gm} (°C)**	**SD (°C)**	**Original T_{CK} (°C)**	**Modified T_{CK} (°C)**
I40-CS25	120	2.12	3.98	5.52	19.78
	130	18.04	3.87	19.16	30.24
	140	29.76	0.47	28.29	36.97
	150	38.96	0.86	35.13	41.88
M40-CS25	120	-4.59	2.24	0.93	16.25
	130	11.97	2.36	16.82	28.59
	140	27.24	4.46	29.38	37.87
	150	35.57	5.01	35.46	42.22
S40-CS25	120	-23.88	0.21	-13.27	-0.77
	130	-13.50	1.05	-1.05	8.91
	140	-4.00	1.67	8.08	15.86
	150	0.83	0.67	12.00	18.77

Chapter 8: Conclusions

8.1 Research summary

This research represents a comprehensive approach to addressing a functional challenge, specifically sugar reduction, in food science. The studies outlined follow a natural progression from model system development and sensory characterization, to identification of key sensory properties impacted by sugar reduction and instrumental predictors of those sensory changes, and finally presents a model for the design of sensory properties through selection of sample composition and processing parameters. While the primary outcome of this work is the mathematical model built by the integration of sensory and thermal sample and ingredient characterization, each study produced some key, stand-alone findings.

The novel use of the Napping-UFP method as a preliminary step in the development of commercially-relevant model systems represents one such contribution (Chapter 3). Key conclusions from research presented in Chapter 4 include the discovery that texture attributes are most significantly impacted by replacement of sugar by sugar alcohols in confectionary systems, as well as the identification of T_g as a promising predictor of sensory texture. For this reason, use of sugar alcohol ingredients with T_g values most similar to that of sucrose (isomalt, maltitol) resulted in reduced sugar samples with sensory properties that most closely matched those of the full-sugar control samples.

The relative congruence of trained panel and consumer evaluations of confectionary sample texture, as well as confirmation of the applicability of trained panelist evaluations to consumer perceptions of tactile and oral stickiness, represents another key finding (Chapter 5). Utilization of two types of descriptive sensory methods, temporal dominance of sensations

(TDS) and check-all-that-apply (CATA), resulted in the delineation of two tiers of stickiness-contributing attributes, and providing deeper insights into the textural facets of sticky perception and highlighting the synergistic benefits of using multiple sensory methodologies (Chapter 5).

The correlation of stickiness-relevant attributes to overall stickiness perception was also evaluated temporally, providing a means of assessing the dynamic association of each texture attribute to total perceived stickiness intensity (Chapter 6). Research described in Chapter 6 also extended the correlation of T_g and sensory texture attributes, presenting a novel application of T_g for the prediction of textural trajectory. Samples in the rubbery state at room temperature were found to follow a textural trajectory from deformable to enveloping, while glassy samples followed a trajectory from brittle to toothpacking.

Empirical corrections to the Couchman-Karasz equation provide a means of increasing the accuracy of T_g prediction for confectionary model systems (Chapter 7). However, it is combination of this enhanced method of system T_g prediction (Chapter 7) with textural prediction based on system T_g (Chapter 6) that yields the most promising result. By combining the insights of both studies, formulation and cook temperature each become tunable variables with predictable effects on confectionary sample texture. This marriage of sensory and materials science approaches to understanding food properties represents the central theme of this dissertation.

8.2 Future work

The potential to create unique confectionary texture profiles through substitution of sucrose by sugar alcohols was discovered (Chapter 4) and utilized (Chapters 5-6) in this

dissertation. Among the most interesting phenomena was the divergence in texture properties of samples made with 25% or 50% substitution of sucrose with mannitol; samples with 25% mannitol exhibited a sticky texture profile, while samples with 50% exhibited a crumbly texture profile due to the presence of crystalline mannitol. We explored only 2 usage levels for each sugar alcohol, so the precise effect of varying mannitol concentrations on physical state and textural attributes of confectionary products is unknown. Future studies could identify the minimum % mannitol to observe crystallization and further investigate shift in confectionary texture profile across a range of mannitol usage levels.

Another particularly interesting finding from this research resulted from the combination of TDS and CATA texture profiles to identify tiers of stickiness-contributing attributes. The layered insights derived from joining data from a temporal method (TDS) with a method allowing multiple attribute selection (CATA) prompted the question of how temporal CATA (TCATA) data would compare to the results from our TDS and CATA studies. While TCATA would allow for temporal assessment of multiple attributes at a time, we wondered if the cognitive load of the TCATA method would alter a panelist's mastication process relative to a natural mastication process. In other words, would panelists chew more slowly or deliberately when they are tasked with evaluating the presence or absence of a list of attributes simultaneously than they normal would under ordinary eating conditions? A comparative study measuring the mastication parameters of subjects participating in a TDS, TCATA, and chewing under ordinary conditions could give insight into whether texture data from temporal sensory tests are true to regular mastication processes and texture perceptions.

The exploration of T_g as a key variable to control in the formulation and processing of confectionary products represents a significant contribution of this work. Promising potential was found for the model systems utilized; however, while the model systems used are representative of commercial confectionary products, they represent a small subsection of confectionary products, and an even smaller subsection of amorphous food products. Therefore, expansion of this approach to broader categories of food systems, particularly other amorphous products with high sugar content such as snack bars or cereals, is merited to confirm or adapt the models and relationships presented here for use with other types of foods.

As discussed in Chapter 6, some caveats must be addressed when applying a constant metric (T_g) for the prediction of a dynamic perception (texture), or when asserting the universality of an individual process (mastication) and perception (sensory texture). In reality, the T_g of a sample directly applies only to the properties of the sample before mastication occurs. Trends in texture perception during mastication can be related to as-is sample T_g, but individual variations in mastication parameters, including differences in the force and rate of chewing or differences in salivation, will also affect perceived texture. Further study of the balance of material properties and individual mastication behaviors towards shaping texture perception would deepen understanding and probe the limitations of T_g as a predictor of texture.

Appendix A: Standard deviation values for Chapter 4 sensory data tables

Table A.1. Standard deviation values for each attribute, grouped by sensory modality, computed for each of the three formula types, corresponding to mean values given in Table 4.4. Sensory ratings for all samples from each formula type were aggregated to produce the standard deviation values shown.

Modality	Attribute	Standard Deviation Values		
		SD*	LD*	LL*
Appearance	Glossy	3.57	2.99	3.40
	Porous	4.18	3.92	3.61
	Bubbled	3.22	2.69	2.45
	Darkness	2.09	2.87	1.69
Aroma	Browned Butter	3.24	3.39	3.14
	Burnt Sugar	3.03	2.92	2.71
	Oxidized	3.27	3.58	3.31
	Butterscotch	3.14	3.01	3.32
Texture	Toothpacking	3.05	3.00	3.04
	Crumbly	4.39	4.35	4.57
	Sticky	3.60	4.57	3.66
	Cohesive	4.04	4.08	4.03
	Force Required to Pierce	3.73	3.98	3.63
Aroma By Mouth	Browned Butter	2.93	2.95	2.38
	Burnt Sugar	3.21	3.62	3.29
	Oxidized	2.75	3.13	3.45
	Molasses-like	3.92	3.07	3.18
	Butterscotch	2.82	3.15	2.50
Taste	Sweet	2.58	2.82	2.81
	Salty	3.37	3.33	3.06
Aftertaste	Sweet	3.29	3.51	3.09
	Burnt Sugar	3.29	3.32	2.69
	Cooked Dairy	3.17	3.68	2.90
	Oily mouthcoating	3.24	3.94	3.39

* SD stands for small-scale dark; LD stands for large-scale dark; LL stands for large-scale light

Appendix A (cont.)

Table A.2. Standard deviation values for each attribute, grouped by sensory modality, computed for each sugar replacer and replacement level, corresponding to mean values given in Table 4.5. Sensory ratings for all samples from each sugar replacement treatment were aggregated to produce the standard deviation values shown.

Modality	Attribute	Standard Deviation Values								
		C0*	I25*	I50*	M25*	M50*	N25*	N50*	S25*	S50*
Appearance	Glossy	3.33	3.36	3.61	3.25	3.06	2.25	3.05	2.67	1.47
	Porous	3.08	2.80	3.52	3.27	3.36	3.66	3.93	3.45	3.27
	Bubbled	4.07	4.08	4.71	4.14	4.53	4.35	4.77	4.84	5.36
	Darkness	3.59	2.78	2.36	2.52	2.52	2.87	2.17	3.04	2.78
Aroma	Browned Butter	3.20	3.43	3.32	3.31	3.47	3.25	3.29	3.33	4.02
	Burnt Sugar	3.36	3.13	2.60	3.06	2.62	3.33	2.82	3.37	3.54
	Oxidized	3.29	3.34	3.63	3.66	3.70	3.10	3.51	3.54	3.78
	Butterscotch	3.08	3.19	3.07	3.03	2.79	2.66	3.32	3.02	3.45
Texture	Toothpacking	2.76	2.77	2.54	2.58	2.69	3.15	3.04	3.16	3.62
	Crumbly	2.39	2.56	2.50	2.45	2.50	3.08	3.22	3.09	0.26
	Sticky	2.23	2.25	2.10	2.27	2.79	2.79	2.50	2.65	2.54
	Cohesive	2.41	2.52	2.57	2.59	2.84	2.03	3.74	2.44	3.25
	Force Required to Pierce	2.77	2.74	2.65	2.71	2.19	2.24	2.57	3.49	3.06
Aroma By Mouth	Browned Butter	3.09	3.25	3.25	3.34	3.46	3.37	2.89	3.27	3.35
	Burnt Sugar	4.36	3.68	4.00	4.03	3.76	3.72	2.81	3.93	3.89
	Oxidized	2.97	3.26	3.47	3.01	3.53	3.40	3.72	3.55	3.52
	Molasses-like	3.91	3.81	3.74	4.04	3.70	3.73	3.00	3.99	4.04
	Butterscotch	3.05	2.96	3.05	3.18	2.83	3.07	2.75	2.76	2.75
Taste	Sweet	2.91	2.68	2.67	2.75	2.79	2.60	2.80	2.77	2.50
	Salty	3.50	3.18	3.26	3.28	3.37	3.26	3.35	3.01	3.30
Aftertaste	Sweet	3.17	3.38	3.11	3.26	3.21	3.28	2.46	3.19	3.39
	Burnt Sugar	4.06	3.23	3.05	3.35	3.31	3.46	2.76	3.58	3.30
	Cooked Dairy	3.39	3.34	3.54	3.53	3.61	3.68	2.95	3.29	3.74
	Oily mouthcoating	3.24	3.41	3.47	3.65	3.24	3.28	3.23	3.29	3.88

* C0 stands for full-sugar control; I stands for isomalt; M stands for maltitol; N stands for mannitol; S stands for sorbitol; 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol

Appendix B: Principal components analysis (PCA) factor loadings for Chapter 4 PCA biplots

Table B.1. Principal components analysis (PCA) factor loadings for aroma (Ar) and aroma by mouth (AMB) attributes. These values correspond to Figure 4.3, a PCA biplot of the first two factors.

Attribute	F1	F2	F3	F4	F5	F6	F7	F8	F9
ArBrownedButter	0.965	0.048	-0.201	0.043	0.038	-0.048	0.143	0.020	0.011
ArButterscotch	0.823	0.256	-0.410	0.261	0.026	0.128	-0.053	0.028	0.004
ArBurntSugar	0.744	-0.589	-0.249	0.015	0.132	-0.098	-0.056	-0.068	-0.046
ArOxidized	-0.594	0.676	0.152	0.209	0.346	0.024	0.037	-0.032	-0.031
ABMButterscotch	0.691	0.284	0.593	0.251	-0.149	-0.014	-0.010	-0.063	0.028
ABMBrownedButter	0.806	0.233	0.497	-0.157	0.122	-0.008	-0.033	0.084	-0.039
ABMMolassesLike	-0.467	-0.786	0.075	0.384	-0.024	-0.076	-0.006	0.073	-0.008
ABMBurntSugar	0.160	-0.927	0.170	-0.064	0.273	0.041	-0.009	-0.005	0.073
ABMOxidized	-0.020	0.962	-0.211	0.007	0.087	-0.125	-0.055	0.025	0.057

Appendix B (cont.)

Table B.2. Principal components analysis (PCA) factor loadings for texture (Tex) attributes. These values correspond to Figure 4.4, a PCA biplot of the first two factors.

Attribute	F1	F2	F3	F4	F5
TexForceRequiredtoPierceSample	0.009	0.872	-0.487	-0.022	-0.031
TexCrumbly	-0.920	0.303	0.129	0.211	0.010
TexSticky	0.982	-0.066	0.063	0.121	-0.111
TexCohesive	0.975	0.037	-0.160	0.100	0.115
TexToothpacking	0.405	0.738	0.537	-0.055	0.017

Appendix C: Standard deviation values for Chapter 4 instrumental data tables

Table C.1. Standard deviation values for water activity (a_w), moisture content expressed in percent wet basis (% wb), onset, midpoint, and endpoint temperatures of the glass transition (T_g), and onset temperature of melting (T_m) of caramel coating samples, corresponding to mean values given in Table 4.6. Instrumental data from both batches of the same formula were combined to produce the standard deviation values shown.

Sample*	a_w	Moisture Content, % wb	T_g onset (°C)	T_g midpoint (°C)	T_g endpoint (°C)	T_m onset (°C)
SD-C0	0.00583	0.209	2.52	2.41	2.20	n/a
SD-I25	0.00249	0.099	0.0768	0.229	0.467	n/a
SD-I50	0.00187	0.126	0.400	0.534	0.752	n/a
SD-M25	0.0156	0.160	0.186	0.403	0.763	n/a
SD-M50	0.00207	0.151	0.479	0.630	1.08	n/a
SD-N25	0.00227	0.092	0.398	0.592	0.870	n/a
SD-N50	0.0241	0.085	1.22	1.44	1.75	6.82
SD-S25	0.00352	0.369	9.70	5.70	3.75	n/a
SD-S50	0.00211	0.212	0.624	0.357	0.195	n/a
LD-C0	0.0141	0.255	0.272	0.321	0.262	n/a
LD-I25	0.0708	0.235	0.669	0.542	0.553	n/a
LD-I50	0.00610	0.257	0.467	0.527	0.744	n/a
LD-M25	0.0695	0.191	1.93	1.70	1.54	n/a
LD-M50	0.00443	0.320	1.39	1.31	1.18	n/a
LD-N25	0.00771	0.380	1.43	1.46	1.58	n/a
LD-N50	0.0458	0.329	2.15	2.25	2.62	2.85
LD-S25	0.0155	0.344	1.28	1.27	1.31	n/a
LD-S50	0.00855	0.323	0.706	0.712	0.694	n/a
LL-C0	0.0274	0.135	1.26	1.53	1.67	n/a
LL-I25	0.00711	0.181	0.967	1.18	1.30	n/a
LL-I50	0.0871	0.126	0.456	0.448	0.571	n/a
LL-M25	0.0115	0.134	2.03	1.09	0.39	n/a
LL-M50	0.00266	0.189	0.624	0.305	0.0714	n/a
LL-N25	0.00703	0.266	0.551	0.342	0.528	n/a
LL-N50	0.00611	0.112	0.624	0.611	0.740	3.03
LL-S25	0.00747	0.235	0.341	0.534	0.874	n/a
LL-S50	0.0857	0.143	0.561	0.479	0.531	n/a

*SD stands for small-scale dark; LD stands for large-scale dark; LL stands for large-scale light; C0 stands for full-sugar control; I stands for isomalt; M stands for maltitol; N stands for mannitol; S stands for sorbitol; 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol

Appendix C (cont.)

Table C.2. Standard deviation values for Texture Profile Analysis parameters of fracturability, hardness, springiness, chewiness, resilience, cohesiveness, and adhesiveness, corresponding to mean values given in Table 4.8. Instrumental data from both batches of the same formula were combined to produce the standard deviation values shown.

Sample*	Fractur-ability	Hardness	Springi-ness	Chewi-ness	Resilience	Cohesive-ness	Adhesive-ness
SD-C0	1.76	21.4	0.196	41.4	0.213	0.243	9.54
SD-I25	7.53	13.8	0.105	22.4	0.0488	0.0242	10.2
SD-I50	3.64	9.85	0.087	17.2	0.0327	0.0213	0.00
SD-M25	18.9	166	0.0544	145	0.0194	0.0451	0.00
SD-M50	54.7	90.4	0.277	135	0.214	0.212	0.00
SD-N25	53.5	118	0.187	85.6	0.183	0.171	60.7
SD-N50	0.10	11.8	0.0699	7.11	0.125	0.205	5.40
SD-S25	0.00	8.20	0.0837	1.96	0.0680	0.070	245
SD-S50	0.00	1.13	0.165	0.273	0.0518	0.110	27.6
LD-C0	33.3	92.0	0.225	98.5	0.199	0.247	33.1
LD-I25	0.00	82.2	0.318	81.3	0.306	0.349	1.22
LD-I50	7.21	20.3	0.301	29.9	0.309	0.327	7.24
LD-M25	0.00	19.9	0.398	23.5	0.242	0.248	12.1
LD-M50	10.2	94.0	0.177	57.8	0.0828	0.121	548
LD-N25	0.00	65.3	0.0543	23.6	0.0564	0.0655	382
LD-N50	0.00	94.0	0.150	43.5	0.145	0.124	3.70
LD-S25	0.00	5.72	0.0756	1.18	0.0682	0.0728	130
LD-S50	0.00	0.0363	0.0680	0.0623	0.0280	0.0989	35.3
LL-C0	6.37	23.2	0.0701	17.2	0.122	0.179	5.65
LL-I25	0.00	14.2	0.0704	12.8	0.0840	0.128	7.43
LL-I50	0.00	91.1	0.135	33.6	0.136	0.151	17.0
LL-M25	17.5	30.8	0.197	14.5	0.199	0.195	43.2
LL-M50	0.00	75.0	0.126	69.0	0.120	0.125	142
LL-N25	0.00	50.0	0.0780	23.7	0.0712	0.0750	9.41
LL-N50	0.00	16.8	0.0609	8.83	0.0922	0.0963	5.86
LL-S25	0.00	13.1	0.0757	5.00	0.0485	0.0432	87.9
LL-S50	0.00	0.512	0.117	0.425	0.0240	0.177	179

*SD stands for small-scale dark; LD stands for large-scale dark; LL stands for large-scale light; C0 stands for full-sugar control; I stands for isomalt; M stands for maltitol; N stands for mannitol; S stands for sorbitol; 25 stands for 25% replacement of sugar with sugar alcohol; 50 stands for 50% replacement of sugar with sugar alcohol

Appendix D: Differential scanning calorimetry data for Chapter 7

Table D.1. Differential scanning calorimetry data, including glass transition (T_g) onset, midpoint, and endpoint values, and change in specific heat capacity at the glass transition (Δc_p) from the first batch each model confectionary system cooked to 120, 130, 140, and 150°C. Two replicates were conducted for each sample at each final cook temperature. Formula code names are defined in Table 7.1.

Formula	Cook Temperature (°C)	Replicate	T_g onset (°C)	T_g midpoint (°C)	T_g endpoint (°C)	Δc_p (J/g/°C)
C0-CS25	120	1	-0.61	3.74	7.93	0.8144
		2	-0.20	4.44	8.91	0.8305
	130	1	16.90	21.84	26.59	0.8043
		2	16.97	21.23	25.48	0.7991
	140	1	29.42	33.34	36.90	0.7975
		2	29.66	33.32	36.97	0.8169
	150	1	43.09	45.48	47.76	0.7698
		2	42.86	45.25	47.58	0.7209
C0-CS50	120	1	-2.60	2.68	7.78	0.7825
		2	-2.79	2.66	7.73	0.8040
	130	1	17.05	21.75	26.36	0.7665
		2	16.18	21.58	26.68	0.8002
	140	1	31.38	35.58	39.49	0.8084
		2	32.00	35.91	39.60	0.8056
	150	1	45.59	48.04	50.50	0.7655
		2	45.58	48.10	50.53	0.7585
I20-CS0	120	1	-7.59	-3.38	0.64	0.8651
		2	-7.48	-3.52	0.31	0.8553
	130	1	10.61	15.34	19.78	0.8858
		2	10.50	15.14	19.54	0.8988
	140	1	24.83	29.29	33.43	0.8596
		2	25.16	29.55	33.77	0.8376
	150	1	33.94	36.57	39.14	0.7243
		2	34.40	37.30	40.01	0.7954
I20-CS25	120	1	-2.59	1.51	5.45	0.8190
		2	-3.38	1.35	5.77	0.8402
	130	1	13.81	18.39	22.75	0.7780
		2	13.64	18.59	23.16	0.7881
	140	1	30.32	35.18	39.70	0.7939
		2	27.98	33.66	38.96	0.7995
	150	1	39.09	42.12	44.90	0.7499
		2	39.93	43.12	45.96	0.7947

Appendix D (cont.)

Table D.1 (cont.)

Formula	Cook Temperature (°C)	Replicate	T_g onset (°C)	T_g midpoint (°C)	T_g endpoint (°C)	Δc_p (J/g/°C)
I20-CS50	120	1	-5.12	-0.86	3.32	0.7929
		2	-1.72	2.65	7.01	0.8118
	130	1	14.96	19.34	23.67	0.7861
		2	14.42	18.93	23.35	0.8249
	140	1	28.58	32.88	36.93	0.8495
		2	27.86	32.75	37.31	0.8697
	150	1	43.31	45.58	47.90	0.7759
		2	44.35	46.79	49.13	0.7821
I40-CS0	120	1	-7.89	-4.19	-0.62	0.9398
		2	-8.72	-4.62	-0.83	0.9559
	130	1	6.88	11.77	16.32	0.9314
		2	7.66	11.93	16.06	0.9379
	140	1	22.01	26.09	30.05	0.7589
		2	21.99	26.23	30.34	0.8942
	150	1	33.32	35.99	38.69	0.9146
		2	33.83	36.50	39.28	0.9193
I40-CS25	120	1	1.29	5.87	10.17	0.8491
		2	0.96	5.23	9.31	0.8756
	130	1	17.16	21.80	26.18	0.8203
		2	16.90	20.95	24.89	0.8092
	140	1	25.35	30.14	34.60	0.8082
		2	25.82	30.18	34.34	0.8031
	150	1	37.42	39.90	42.30	0.7974
		2	37.36	39.44	41.82	0.7839
I40-CS50	120	1	-0.21	4.51	8.96	0.8765
		2	0.05	4.29	8.42	0.8773
	130	1	14.50	19.89	25.06	0.8556
		2	15.95	20.74	25.42	0.8098
	140	1	28.77	32.76	36.48	0.8291
		2	28.65	32.51	36.23	0.8830
	150	1	39.68	41.99	44.20	0.8144
		2	40.31	42.84	45.27	0.8067
M20-CS0	120	1	-11.09	-7.14	-3.22	0.8386
		2	-10.93	-6.76	-2.62	0.6997
	130	1	-0.83	5.34	11.00	0.9122
		2	0.27	5.30	10.20	0.7318
	140	1	11.37	16.25	21.04	0.8463
		2	11.75	16.36	20.80	0.7599
	150	1	20.86	25.65	30.42	0.9076
		2	22.08	26.52	30.77	0.7927

Appendix D (cont.)

Table D.1 (cont.)

Formula	Cook Temperature (°C)	Replicate	T_g onset (°C)	T_g midpoint (°C)	T_g endpoint (°C)	Δc_p (J/g/°C)
M20-CS25	120	1	-8.30	-3.52	0.96	0.7805
		2	-8.13	-3.20	1.57	0.7797
	130	1	2.30	7.21	11.82	0.8324
		2	2.87	7.79	12.34	0.7865
	140	1	15.58	20.53	25.33	0.7700
		2	15.29	20.62	25.67	0.7911
	150	1	31.46	34.32	36.95	1.1960
		2	28.28	32.78	37.17	0.6774
M20-CS50	120	1	-12.87	-8.44	-4.03	0.7818
		2	-13.98	-9.06	-4.28	0.8540
	130	1	-0.55	4.75	9.93	0.7612
		2	-1.53	4.07	9.52	0.8367
	140	1	12.01	18.50	24.74	0.8472
		2	12.96	18.64	24.17	0.7957
	150	1	18.72	24.64	30.38	0.7908
		2	18.66	23.80	28.92	0.7848
M40-CS0	120	1	-16.79	-13.01	-9.35	0.8430
		2	-16.90	-12.57	-8.43	0.8676
	130	1	1.15	5.47	9.60	0.8178
		2	1.82	5.46	9.11	0.7868
	140	1	17.51	22.26	26.92	0.8265
		2	18.44	23.74	28.73	0.7651
	150	1	33.80	36.35	38.78	0.7890
		2	33.06	35.75	38.24	0.7155
M40-CS25	120	1	-7.23	-2.75	1.48	0.8339
		2	-6.44	-2.55	1.27	0.8607
	130	1	8.48	13.62	18.52	0.8514
		2	9.32	14.36	19.20	0.7954
	140	1	26.42	31.00	35.32	0.8302
		2	26.35	31.19	35.59	0.8104
	150	1	37.34	39.95	42.32	0.7516
		2	37.58	39.87	42.08	0.7452
M40-CS50	120	1	-7.93	-3.00	1.75	0.8288
		2	-7.44	-3.03	1.25	0.7754
	130	1	6.37	11.49	16.35	0.7915
		2	7.34	11.95	16.35	0.7536
	140	1	23.35	29.30	35.06	0.7399
		2	23.06	28.99	34.58	0.7631
	150	1	35.01	37.58	40.66	0.6916
		2	34.85	38.21	41.48	0.7283

Appendix D (cont.)

Table D.1 (cont.)

Formula	Cook Temperature (°C)	Replicate	T_g onset (°C)	T_g midpoint (°C)	T_g endpoint (°C)	Δc_p (J/g/°C)
S20-CS0	120	1	-16.94	-11.81	-6.79	0.7115
		2	-17.04	-11.58	-6.37	0.6120
	130	1	-5.36	1.27	7.62	0.8458
		2	-2.85	2.45	7.69	0.7211
	140	1	9.32	15.03	20.55	0.7445
		2	8.68	14.42	19.96	0.8210
	150	1	19.34	25.34	31.12	0.8413
		2	20.98	25.99	30.84	0.8349
S20-CS25	120	1	-21.46	-16.57	-11.77	0.8013
		2	-20.49	-16.13	-11.84	0.7557
	130	1	-5.48	0.35	6.01	0.7856
		2	-4.42	0.91	6.14	0.7675
	140	1	6.77	12.58	18.27	0.8045
		2	6.40	12.61	18.61	0.8356
	150	1	11.16	17.21	23.12	0.7868
		2	13.12	18.68	24.14	0.7228
S20-CS50	120	1	-21.16	-15.67	-10.20	0.7234
		2	-20.14	-14.23	-8.50	0.7852
	130	1	-6.92	-0.05	6.60	0.8030
		2	-6.46	0.11	6.30	0.7998
	140	1	3.64	9.03	14.77	1.3990
		2	4.73	12.32	19.69	0.7945
	150	1	10.08	17.63	24.82	0.7732
		2	11.15	18.73	26.19	0.7752
S40-CS0	120	1	-51.82	-48.03	-44.48	0.5313
		2	-50.57	-46.33	-42.33	0.5334
	130	1	-36.74	-22.60	-9.21	0.7761
		2	-27.24	-18.54	-10.40	0.8218
	140	1	-11.56	-5.26	0.79	0.9048
		2	-12.99	-5.39	1.98	0.9190
	150	1	-8.92	-0.27	7.78	0.9155
		2	-7.38	-0.09	6.80	0.7897
S40-CS25	120	1	-29.29	-23.73	-18.40	0.9246
		2	-29.75	-24.18	-18.82	0.9112
	130	1	-18.57	-12.60	-6.92	0.9082
		2	-18.46	-12.58	-7.01	0.8960
	140	1	-9.70	-2.69	3.91	0.9257
		2	-9.58	-2.43	4.35	0.9173
	150	1	-6.39	1.33	8.66	0.9155
		2	-6.21	1.21	8.33	0.9028

Appendix D (cont.)

Table D.1 (cont.)

Formula	Cook Temperature (°C)	Replicate	T_g onset (°C)	T_g midpoint (°C)	T_g endpoint (°C)	Δc_p (J/g/°C)
S40-CS50	120	1	-35.15	-29.11	-23.31	0.9371
		2	-33.53	-27.63	-21.95	0.9017
	130	1	-20.86	-14.85	-9.05	0.8843
		2	-20.97	-14.88	-9.01	0.9114
	140	1	-13.06	-6.67	-0.32	0.8886
		2	-13.89	-6.49	0.59	0.9147
	150	1	-8.39	-0.31	7.34	0.9306
		2	-8.66	-0.11	7.82	0.8818

Appendix E: Equation coefficients and R^2 values for Chapter 7

Table E.1. Linear equation coefficients, where y = mx + b, and R^2 values, describing the relationship between moisture content (x) and T_{gm} (y) and corresponding to Figure 7.5, for each individual sample. Formula code names are defined in Table 7.1.

Formula	m	b	R^2
C0-CS25	-4.82	60.1	0.993
C0-CS50	-5.93	51.4	0.994
I20-CS0	-4.25	40.4	0.952
I20-CS25	-5.17	50.1	0.977
I20-CS50	-5.44	47.2	0.992
I40-CS0	-4.53	40.0	0.997
I40-CS25	-3.73	41.6	1.00
I40-CS50	-4.87	43.6	0.973
M20-CS0	-3.82	34.3	0.971
M20-CS25	-4.57	40.1	0.963
M20-CS50	-4.15	26.9	0.990
M40-CS0	-6.13	47.0	0.990
M40-CS25	-4.94	45.4	0.998
M40-CS50	-5.02	41.0	0.949
S20-CS0	-3.89	30.5	0.983
S20-CS25	-3.45	22.1	0.975
S20-CS50	-3.91	24.7	0.995
S40-CS0	-5.22	5.13	0.959
S40-CS25	-2.92	0.808	0.989
S40-CS50	-2.89	-0.678	0.989

Table E.2. Polynomial equation coefficients, where $y = ax^2 + bx + c$, linear equation coefficients, where $y = mx + b$, and R^2 values, describing the relationship between cook temperature minus 120°C (x) and T_{gm} (y) and corresponding to Figure 7.6, for each individual sample. Formula code names are defined in Table 7.1.

	Polynomial Model				Linear Model		
Formula	a	b	c	R^2	m	b	R^2
C0-CS25	-0.0135	1.76	4.38	0.998	1.36	5.74	0.990
C0-CS50	-0.0167	2.00	2.83	1.00	1.50	4.50	0.990
I20-CS0	-0.0279	2.19	-3.56	1.00	1.35	-0.764	0.967
I20-CS25	-0.0222	2.06	1.10	0.998	1.40	3.32	0.978
I20-CS50	-0.0122	1.86	1.11	0.999	1.50	2.33	0.994
I40-CS0	-0.0154	1.83	-4.52	1.00	1.36	-2.98	0.990
I40-CS25	-0.0158	1.59	5.94	0.995	1.11	7.52	0.979
I40-CS50	-0.0153	1.72	4.45	1.00	1.26	5.99	0.988
M20-CS0	-0.00620	1.29	-6.95	1.00	1.10	-6.32	0.997
M20-CS25	0.00530	1.08	-3.48	1.00	1.24	-4.00	0.998
M20-CS50	-0.0188	1.69	-9.23	0.993	1.13	-7.35	0.972
M40-CS0	-0.0130	2.03	-13.0	1.00	1.64	-11.7	0.995
M40-CS25	-0.0196	2.03	-3.09	0.996	1.45	-1.13	0.982
M40-CS50	-0.0150	1.85	-3.58	0.994	1.40	-2.09	0.985
S20-CS0	-0.0065	1.45	-11.8	1.00	1.25	-11.1	0.998
S20-CS25	-0.0291	2.02	-16.4	1.00	1.15	-13.5	0.951
S20-CS50	-0.0187	1.66	-14.9	1.00	1.10	-13.0	0.977
S40-CS0	-0.0537	3.17	-47.1	1.00	1.56	-41.8	0.914
S40-CS25	-0.0188	1.42	-24.2	0.997	0.857	-22.3	0.960
S40-CS50	-0.0178	1.46	-28.2	0.999	0.928	-26.4	0.970

Appendix F: Linear trendlines for T_{gm} vs final cook temperature

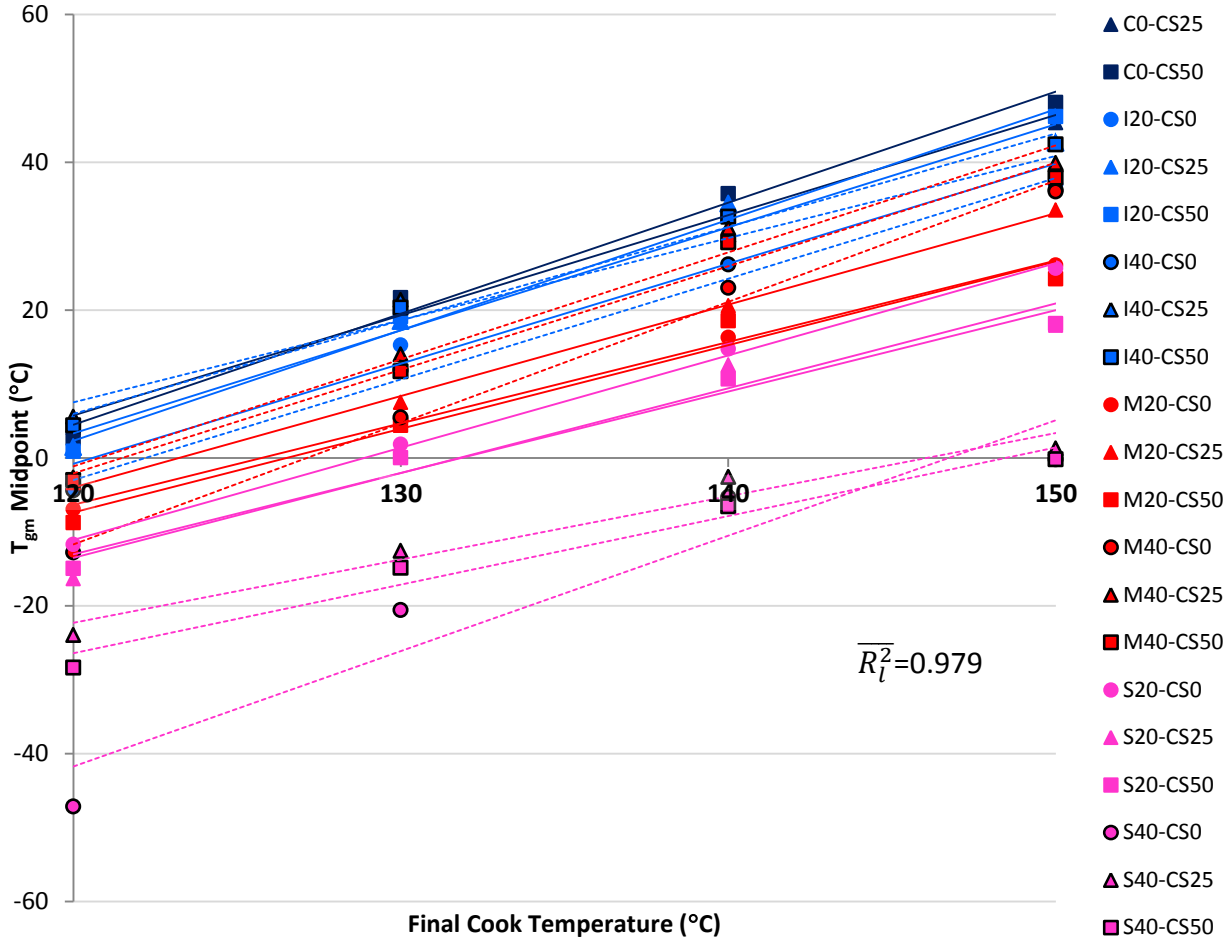

Figure F.1. Plot of average measured T_{gm} midpoint values versus final cook temperature for all samples with linear trendlines. The average R^2 for the linear (R_l^2) trendline of each sample is given. Solid trendlines correspond to 20% sugar alcohol formulas, while dashed trendlines correspond to 40% sugar alcohol formulas. Formula code names are defined in Table 7.1.